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RESIDUE REVIEWS

Rückstands-Berichte

Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds

Rückstände von Pesticiden und anderen Fremdstoffen in Nahrungs- und Futtermitteln

Edited by
Francis A. Gunther
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with the co-operation
of numerous experts

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Contents: Introduction to symposium—Special features in the analysis of pesticide residues: Residue analysis and food control. Gas chromatography using an electron absorption detector. Quantitative determination of pesticide residues by electron absorption chromatography. Characteristics of the detector. Selective detection and identification of pesticide residues. Applications of the microcoulometric titrating system as a detector in gas chromatography of pesticide residues. Comparison of flame ionization and electron capture detectors for the gas chromatographic evaluation of herbicide residues. Applications of polarography for the detection and determination of pesticides and their residues. Polarography for the determination of organic feed medicaments. The potential of fluorescence for pesticide residue analysis. Infrared and ultraviolet spectrophotometry in residue evaluations. Automatic wet chemical analysis as applied to pesticide residues. Determination of pesticide residues by neutron-activation analysis.

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1. Sully, B. D., *Analyst*, 1962, **87**, 940-3.

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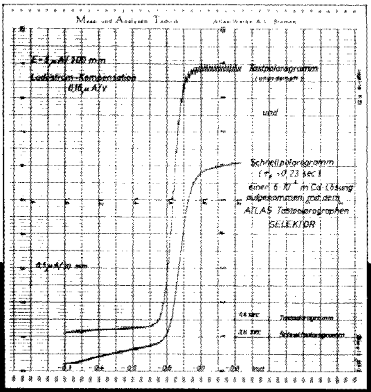
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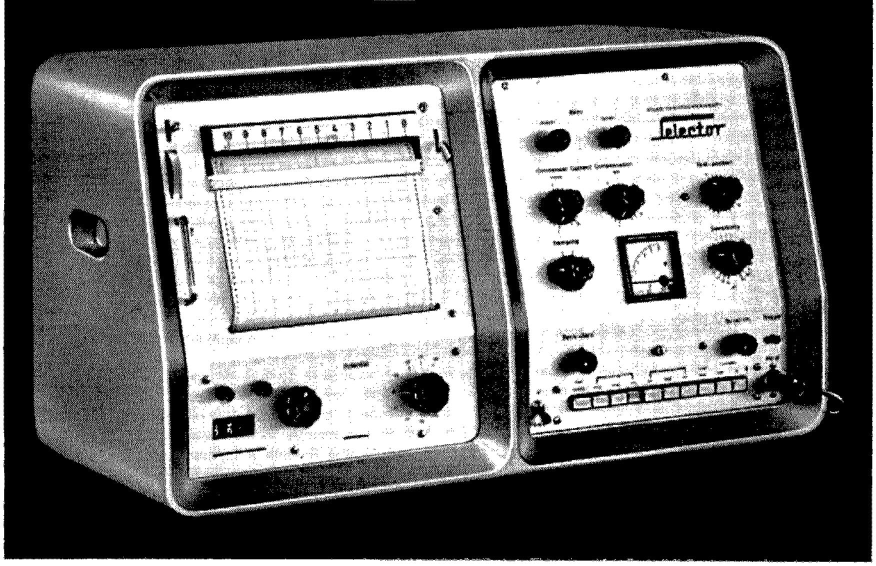
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SUMMARIES FOR CARD INDEXES

IZAAK MAURITS KOLTHOFF: JAMES J. LINGANE, *Talanta*, 1964, **11**, 67.

The status of and trends in analytical chemistry: I. M. KOLTHOFF, *Talanta*, 1964, **11**, 75.

Determination of uranium at microgram levels by derivative polarography: C. AUERBACH and G. KISSEL, *Talanta*, 1964, **11**, 85. (Brookhaven National Laboratory, Associated Universities, Inc., Upton, L.I., New York, U.S.A.)

Summary—The incremental method of derivative polarography has been applied to the low-level analysis of uranium in acetate-buffered EDTA electrolyte. Optimum conditions are shown for the rapid determination of $2 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ bismuth and of $5 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ molybdenum, with a precision $\leq 2\%$ and without prior separation. Uranium in amounts $\leq 10\ \mu g$ may be detected in a 10^4-fold excess of bismuth. The method has been used successfully for the analysis of a bismuth alloy containing $0{\cdot}1\%$ of uranium.

Properties of bases in acetonitrile as solvent—III: Hydrogen bonding between protonated and free nitrogen bases: J. F. COETZEE and G. R. PADMANABHAN with G. P. CUNNINGHAM, *Talanta*, 1964, **11**, 93. (Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pennsylvania, U.S.A.)

Summary—In acetonitrile as solvent, the stronger nitrogen bases, B, form 1:1 and also higher hydrogen-bonded complexes with their conjugate acids, BH^+. Formation constants for these complexes have been determined by glass-electrode measurements in buffer solutions consisting of a constant concentration of the perchlorate or picrate of the base and varying concentrations of free base. The results show that the degree of complexation increases with increasing strength of the base and increasing number of hydrogen atoms in the ammonium group of the conjugate acid, and also that it has severe steric requirements, as expected. Thus, complexation is most extensive for the lower aliphatic primary amines and aliphatic cyclic secondary amines, such as piperidine, and does not occur with non-cyclic tertiary amines, except trimethylamine. The significance of these complexation reactions in potentiometric and conductimetric titrations and in studies concerned with the relative strength of bases is discussed.

ИЗАК МОРИЦ КОЛЬТГОФ: JAMES J. LINGANE, *Talanta*, 1964, **11**, 67.

СОСТОЯНИЕ И НАПРАВЛЕНИЯ В АНАЛИТИЧЕСКОЙ ХИМИИ: I. M. KOLTHOFF, *Talanta*, 1964, **11**, 75.

ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ УРАНА МЕТОДОМ ДЕРИВАТИВНОЙ ПОЛЯРОГРАФИИ: CLEMENS AUERBACH and GEORGE KISSEL, *Talanta*, 1964, **11**, 85.

Резюме—Описан полярографический метод для определения малых количеств урана при помощи электролита состалшего из этилендиамитетрауксусной кислоты и буфферного уксуснокислого раствора. Показаны оптимальные условия для быстрого определения количеств урана порядком 10^{-6}М в присутствии висмута и молибдена (0,01 М) с ошибкой = 2% без предварительного разделения. Передложеный метод был успешно применен для анализа висмутного сплава содержащего 0,1% урана.

СВОЙСТВА ЩЕЛОЧЕЙ В АЦЕТОНИТРИЛЕ В КАЧЕСТВЕ РАСТВОРИТЕЛЯ III. ВОДОРОДНЫЙ СВЯЗ МЕЖДУ ЩЕЛОЧАМИ СОДЕРЖАЩИМИ ПРОТОН И НЕСОДЕРЖАЩИМИ ВОДОРОД: J. F. COETZEE and G. R. PADMANABHAN with G. P. CUNNINGHAM, *Talanta*, 1964, **11**, 93.

Резюме—В ацетонитриле в качестве растворителя образует более сильное азотистое основание с соответствующими кислотами комплекси BH^+ в соотношении 1:1, и с более высоким содержанием водорода. Константы образования этих комплексов определялись с помощю стеклянного электрода в буфферных ростворах содержащих постоянную концентрациию перхлората или пикрата соответствующего основания и различные концентрации свободного основания. Резултаты показивают, что степень комплексообразования возрастает с увеличением силы основания и возрастанием количества атомов водорода в аминогруппах связывающей кислоты. Необходимо учитывать тоже вопрос стерических препятствый. Комплексообразование наиболее сильно для более низких алифатических первычных аминов и для алифатических циклических вторичных аминов, на пр. пиперидин и не возможно для нециклических третичных аминов с исключением триетиламина. Обсуждается значение подобных комплексообразовательных реакций для потенциометрического и кондуктометрического титрования и для исследования относительной силы оснований.

A.C. polarographic studies on the influence of tensammetric waves on reduction waves of inorganic cations and *vice versa:* S. L. Gupta and S. K. Sharma, *Talanta*, 1964, **11**, 105. (Department of Chemistry, Birla College, Pilani, Rajasthan, India.)

Summary—This investigation deals with the studies on the effect of the nature and concentration of surface active substances (s.a.s) on the a.c. reduction peaks of Cd^{2+} and Zn^{2+} ions and *vice-versa* by a.c. polarography. The magnitude of the reduction peak is not influenced up to a certain concentration of the s.a.s., but with concentrations higher than this, the magnitude of the reduction peak progressively decreases; a concentration of 1·3% of n-amyl alcohol completely removes the $10^{-3}M$ Cd^{2+} peak. Neither magnitude nor the peak potential of the tensammetric peak of n-amyl alcohol are influenced by the presence of Cd^{2+} ions. There is a linear relation between the concentration of the electroactive species and the optimum concentration of the s.a.s., and also the concentration of the s.a.s. just required to remove the reduction peak. These observations are further supported by the curve which gives the linear relation between the concentration of the electroactive species and the amount of the s.a.s. required to reduce the magnitude of the reduction peak to half its value. The amount of the surfactants required to remove the reduction peak completely is in the order n-amyl alcohol > Cerfak [Sodium naphthalene (2-dodecyl) 3-sulphonate] > cetylpyridinium bromide. These results are discussed.

Some temperature effects in gas chromatography: W. E. Harris and H. W. Habgood, *Talanta*, 1964, **11**, 115 (Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.)

Summary—The expected effects of temperature on column efficiency are considered in detail for typical compounds of low, intermediate and high retention. Situations involving various relative values of the resistances to mass transfer in the gas and liquid phases are analysed. One conclusion reached is that flow conditions cannot be chosen at any one temperature which will result in maximum efficiency for all solutes. It would also be expected that column efficiency generally should increase with increasing temperature although under some conditions, of high mass transfer resistances in the liquid phase relative to that in the gas phase, a decrease or virtual independence of temperature may be found. The effect of variation of column temperature on pressure drop across the column is also examined briefly.

ПОЛЯРОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ (ПЕР. ТОКОМ) ВЛИЯНИЯ ТЕНСАММЕТРИЧЕСКИХ ВОЛН НА ПИКИ РЕДУКЦИИ НЕОРГАНИЧЕСКИХ КАТИОНОВ И НАОБОРОТ:

S. L. Gupta and S. K. Sharma, *Talanta*, 1964, **11**, 105.

Резюме—Было проведено изучение влияния природы и концентрации поверхностно активных веществ на пики редукции Cd^{2+} и Zn^{2+} и наоборот при помощи полярографии переменным током. Ясно, что величина пика редукции не зависит до определенной концентрации п.а.в. от их концентрации, но при дальнейшом увеличении концентрации величина пика редукции значительно уменшается /при 1,3% —амилалкогола совершенно исчезает пик 10^{-3}M Cd^{2+}/. Величина и потенциал тенсамметрического пика n-амилалкогола неподвергаются влиянию Cd^{2+}. Существует прямая зависимость между концентрацией электроактивного вещества и оптимумом концентрации п.а.в подобно тому как концентрация п.а.в. требуется для устранения пика редукции. Эти наблюдения потверждаются кривой, которая дает прямую зависимость между концентрацией электроактивного вещества и количеством п.а.в. необходимом для уменшения величины пика редукции на половину. Количество п.а.в. требуемое для совершеного исчезновения пика редукции находится в ряду n-амилалкогол > церфаг > цетилпиридиниум вромид. Эти результаты обсуждаются в данной статье.

НЕКОТОРЫЕ ТЕМПЕРАТУРНЫЕ ЗФФЕКТЫ В ГАЗОВОЙ ХРОМАТОГРАФИИ:

W. E. Harris and H. W. Habgood, *Talanta*, 1964, **11**, 115.

Резюме—Было исследовано влияние температуры на действие колонны для разделения соединений с низкой, средней и высокой ретенцией. Анализируются различные положения включая сопротивления переносу материи в газовой и жидкой фазах. Было установлено, что условия протекания нельзя выбирать для любой температуры, при которой действие для всех веществ в растворе максимальным. Можно также ожидать, что действие колонны может возрастать с возрастом температуры. Наоборот, когда сопротивление транспорта материи в жидкости высоко по сравнению с сопротивлением в газу, можно наблюдать понижение или независимость действия от температуры. Было исследовано тоже влияние температуры на падение давления на колоне.

Thermometric titrations in acetonitrile: E. J. Forman and D. N. Hume, *Talanta*, 1964, **11,** 129. (Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge 39, Mass., U.S.A.)

Summary—The use of acetonitrile as a medium for thermometric acid-base titrations has been studied. Satisfactory titrations are obtainable for a wide variety of amines and organic acids, but the instability of the solvent in the presence of strong bases greatly limits its practical applicability. Data are given on the heats of neutralisation of various acids in acetonitrile, and the results for *m*- and *p*-substituted benzoic acids are shown to correlate well with their Hammett σ-values.

Polarography of copper in diethylenetriaminepenta-acetic acid solutions: E. Jacobsen and G. Kalland, *Talanta*, 1964, **11,** 139 (Chemical Institute A, University of Oslo, Blindern, Norway.)

Summary—The polarographic behaviour of copper in the presence of excess DTPA has been studied by means of the dropping mercury electrode. In an acidic medium the copper^{II} complex is reversibly reduced to the amalgam. At pH values above 5 the wave is broken into two parts and a new irreversible wave appears at a more negative potential. An increase in pH of the supporting electrolyte results in an increase of the second wave at the expense of the original one, the limiting current of the total wave remaining constant. The effect of temperature, pressure of mercury, pH and the concentration of DTPA on the limiting current and the half-wave potentials of the two waves have been investigated and the stability constant of the copper-DTPA complex has been redetermined. The double wave is assumed to be the result of an inhibited electrode reaction, the inhibition being caused by the deposition of the reduction product at the electrode surface. When the applied potential is increased above $-0{\cdot}7$ V *vs.* S.C.E., the film is desorbed and the current rises to its original value.

Geometry-related errors in instrumental neutron-activation analysis: Ralph A. Johnson, *Talanta*, 1964, **11,** 149. (Shell Development Company, Emeryville, California, U.S.A.)

Summary—Geometry-related errors in instrumental neutron-activation analysis are defined and evaluated. Neutron-flux distributions, variations in counting geometry, and intra-sample neutron moderation and reflection are discussed in relation to these errors. Devices for error control are described.

ТЕРМОМЕТРИЧЕСКИЕ ТИТРОВАНИ В СРЕДЕ АЦЕТОНИТРИЛА: Earl J. Forman and David N. Hume, *Talanta*, 1964, **11**, 129.

Резюме—Исследовалось использование ацетонитрила в качестве среды для термометрического кислотнощелочного титрования. Удовлетворительное титрования были получены для большого количества амминов и органических кислот. Однако неустойчивость растворителя в присутствии сильных основании значительно ограничивает его практическое применение. Приведены данные тепла нейтрализации различных кислот в ацетонитриле и результаты соответствуют для м-и паразамещеных бензоловых кислот величинам σ Гаммета.

ПОЛЯРОГРАФИЯ МЕДИ В РАСТВОРАХ ДИЭТИЛЕНЕТРИАМИНЕПЕНТАУКСУСНОЙ КИСЛОТЫ: Einar Jacobsen and Gunnar Kalland, *Talanta*, 1964, **11**, 139.

Резюме—Было исследовано полярографическое поведение меди в присутствии избытка ДТПА при помощи капельного ртутного электрода. В кислой среде комплекс Cu^{2+} обратно восстановливается в амальгаму. При величинах pH больше 5 волна разбивается на две части и необратная волна появляется с больше отрицательным потенциалом. Возрастание pH соответствуюшего злектролита вызивает увеличение второй волны защет исходной волны. Лимитующий ток общей волны остается постоянным. Изучалось влияние температуры, давления ртути, pH и концентрации ДТПА на лимитирующий ток и на полуволновые потенциалы этих двух волн. Так же была определена константа устойчивости комплекса Cu ДТПА. Предполагается что двойная волна является результатом ингибируемой электродной реакции, ингибиция которой была вызвана перемещением продуктов восстановления на поверхности электрода. При возрастании потенциала больше чем —0,7 в /против насищ.к.э./ пленка десорбируется и ток увеличивается до первоначальной величины.

ГЕОМЕТРИЧЕСКИЕ ОШИБКИ В НЕЙТРОННОМ АКТИВАЦИОННОМ АНАЛИЗЕ: Ralph A. Johnson, *Talanta*, 1964, **11**, 149.

Резюме—Были оценены ошибки нейтронного активационного анализа возникающие в результате геометрических факторов. Обсуждаются именно разложение потока нейтронов, варияции геометрии счета, внутренная модерация нейтронов в облучаемом образце, в отношении к ошибкам анализа. Передложен метод определения возникающих ошибок.

Bivalent thallium and the mechanism of the electrode reaction $Tl^{3+} + 2e \rightleftharpoons Tl^+$: H. A. Catherino and Joseph Jordan, *Talanta*, 1964, **11**, 159. (Department of Chemistry, Pennsylvania State University, University Park, Pa., U.S.A.)

Summary—The thallium^{I}-thallium^{III} electrode reaction has been studied by hydrodynamic voltammetry at platinum anodes and cathodes. Conclusive evidence is presented that the electro-oxidation of the aquo ion Tl^+ and the electroreduction of Tl^{3+} proceed via a bivalent thallium species. Thallium^{II} is a stronger oxidant than thallium^{III} ion. In 1*M* aqueous perchloric acid the rate of the disproportionation process

$$2Tl^{II} \rightarrow Tl^+ + Tl^{3+}$$

is relatively fast compared to the electron transfer steps

$$Tl^{II} + e \rightarrow Tl^+$$

$$Tl^{3+} + e \rightarrow Tl^{II}.$$

Polarographic determination of certain medicinal compounds containing dichloracetamido groups: Clark A. Kelly, *Talanta*, 1964, **11**, 175. (Sterling-Winthrop Research Institute, Rensselaer, New York, U.S.A.)

Summary—A polarographic study has been made of a variety of compounds containing dichloracetamido groups, including *N*-(2,4-dichlorobenzyl)-*N*-(2-hydroxyethyl)dichloracetamide (chlorbetamide), *N*-(4-methylsulphonylphenyl)-1,3-dihydroxy-2-propyldichloracetamide (racеophenidol), *N*,*N*′-bis-(2-ethoxyethyl)-*N*,*N*′-*p*-xylylene-bis-dichloracetamide (teclozan), *N*,*N*′-octamethylene-bis-dichloracetamide and their corresponding analogues. Analytical results are discussed from a quantitative and qualitative point of view with special emphasis on the stability of the compounds at various pH and the effect of various elements or groups in the molecule on the half-wave potentials of the two resulting cathodic waves.

ДВУХВАЛЕНТНЫЙ ТАЛЛИЙ И МЕХАНИЗМ ЭЛЕКТРОДНОЙ РЕАКЦИИ $\mathrm{Tl}^{3+} \overset{2e}{\rightleftharpoons} \mathrm{Tl}^{+}$: H. A. Catherino and Joseph Jordan, *Talanta*, 1964, **11**, 159.

Резюме—Изучалась электродная реакция одно- и трехвалентного таллия при помощи гидродинамической волтамметрии на платиновых аноде и катоде. Доказывается что окисление одновалентного и восстановление трехвалентного таллия проходит через двухвалентный таллий. Tl/II/ является более сильным окислителем чем Tl^{3+}. В растворах 1M надхлористой кислоты степень диспропорционации:

$$2\,\mathrm{Tl}\,/\mathrm{II}/ \rightarrow \mathrm{Tl}^{+} + \mathrm{Tl}^{3+}$$

Скорость этой реакции относительно больше по сравнению с отдельными реакциями переноса электронов:

$$\mathrm{Tl}/\mathrm{II}/ + e \rightarrow \mathrm{Tl}^{+}$$

$$\mathrm{Tl}^{3+} + e \rightarrow \mathrm{Tl}/\mathrm{II}/.$$

ПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НЕКОТОРЫХ ЛЕКАРСТВ СОДЕРЖАЩИХ ДИХЛОРОАЦЕТАМИДОВЫЕ ГРУППЫ: Clark A. Kelly, *Talanta*, 1964, **11**, 175.

Резюме—Было проведено полярографическое изучение различных соединений содержащих дихлорацетамидовые группы именно И-/2,4-дихлорбензил/-И-/2-гидроксиэтил/дихлорацетамид/хлорбетамид/, И-/4-метилсульфонфенил/-1, 3-дигидрокси-2-пропилдихлорацетамид/рацеофенидол/, И,И'-бис-/2-этоксиэтил/ -И,И'-р-ксилен-бис-дихлороацетамид/теклозан/, И,И'-октаметилен-бис-дихлорацетамид и их соответствующие аналоги. Обсуждаются аналитические результаты с точки зрения количества и качества. Особое внимание обращается на устойчивость этих соединений при различных pH и влияние различных элементов или групп в молекуле на потенциали полуволны двух результирующих катодических волн.

Schiff base complexes: A numerical study of the nickel^{II}-pyruvate-glycinate system using a high speed computer: D. L. Leussing, *Talanta*, 1964, **11**, 189. (McPherson Chemical Laboratory, Ohio State University, Columbus, Ohio, U.S.A.)

Summary—A numerical study of the nickel^{II}-pyruvate-glycinate system is undertaken and a computer method of solving the pertinent equations is developed. Theoretical titration curves using trial constants are calculated for conditions corresponding to those used experimentally. The observed inter-relationships between the values of the constants, the concentrations of the reactants and the resulting titration curves yield valuable information regarding the importance of the various mixed complexes under the differing conditions. The "best" set of constants which fits the experimental data according to the minimum value of the sum of the squares of the residuals, $pH_{calc}\ i - pH_{obs}\ i$, is obtained. The results of the study lead to a procedure which should be applicable to determining the constants for mixed complex systems in general.

Potentiostatic determination of kinetic parameters of electrode reactions with generation of a reactant *in situ*: Y. Okinaka, S. Toshima and H. Okaniwa, *Talanta*, 1964, 11, 203. (Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai, Japan.)

Summary—It is shown that kinetic parameters of simple, fast electrode reactions of the type $O + ne = R$, where R is soluble in the solution or in the mercury electrode, can be determined by the potentiostatic method with a solution initially containing only the substance O, the substance R being generated *in situ* during electrolysis, provided that the electrode reaction involves only a single rate-determining step. Current-time curves are recorded with a fast response, electronic potentiostat and an oscilloscope upon applying a potential step from the zero-current potential to various potentials on the ascending part of the current-potential curve. The forward rate constant k_f at a given potential is calculated from the current at zero time found by extrapolation of the linear portion of the plot of current against square root of time, while the backward rate constant k_b is calculated indirectly from the slope of the same straight line. Plotting log k_f and log k_b against potential allows a simultaneous determination of the formal standard rate constant k_s, both cathodic and anodic transfer coefficients, the number of electrons involved in the rate-determining step and the formal standard potential of the system being studied. This method is considerably simpler than the well-known Gerischer-Vielstich method, and it should be particularly advantageous when R is highly reactive or forms an amalgam which is unstable in air. The upper limit of k_s that can be determined by this method is the same as that determinable by the Gerischer-Vielstich method. The kinetic parameters found by the present method for the electrode reactions zinc ion-zinc amalgam in $1M$ potassium nitrate, copper^{II} ion-copper amalgam in $1M$ potassium nitrate and cadmium ion-cadmium amalgam in $0{\cdot}5M$ sodium sulphate were in fair agreement with the values reported in the literature.

КОМПЛЕКСЫ ШЕЛОЧЕЙ ТИПА ШИФА: ИССЛЕДОВАНИЕ СИСТЕМЫ НИЕЛЬ (II)-ПИРУВАЛАТ-ГЛИЦИНАТ ПРИ ПОМОЩИ БСТРОГО СЧЕТЧИКА: D. L. LEUSSING, *Talanta*, 1964, **11**, 189.

Резюме—Описано изучение с помощью математических методов системы Ni /2+/—пирувалат—глицинат. Разработан метод решения соответствующих уравнений с помощью счетчика. Были расчитаны теоретические кривые титрования с помощью констант реакции для условий соответствующих экспериментальным. Обнаруженые взаимоотношения между величинами констант концентрации реагентов и полученными кривыми титрования поскитли ценные информации относительно различных смешанных комплексов в различных условиях. Был получен «найлучший» подбор констант который соответствует экспериментальным данным в соответствии с методом наименьших квадратов /$\mathrm{pH}_{\text{рассчит.}}$ и $\mathrm{pH}_{\text{наблюд.}}$/. Результаты изучения позволили разработать общий метод определения констант для систем смешаных комплексов.

ПОТЕНЦИОСТАТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КИНЕТИЧЕСКИХ ПАРАМЕТРОВ ЭЛЕКТРОДНЫХ РЕАКЦИЙ ПОДГОТОВКОЦ РЕАГЕНТА: Y. OKINAKA, S. TOSHSMA and H. OKANIWA, *Talanta*, 1964, **11**, 203

Резюме—Было показано, что кинетические параметры простой и быстрой электродной реакции типа $O + ne = R$, /где R растворяется в ртутом электроде или в растворе/ могут быть олределены с помощью потенциостатического метода при использовании раствора первоначально содержащего только вещество O. Вещество R может быть образовано *in situ* во время злектролиза при условии, что электродная реакция включает только одну степень определящую скорость. Кривые типа ток-час записиваются при помощи быстрого электронического потенциостата и осцилоскопа, причем потенциал накладывается начиная от нулевого тока. Константа k_f при данном потенциале расчитывается из тока при нулевом времени, найденном иутем экстраполирования линеярного участка графика зависимости тока от квадратного корня времени. В то время константа k_b расчитывается ненепосредственно из наклона той же самой прямой линии. Вынося log k_f, log k_b против потенциалу можно проводит одновременно определение константы k_s, катодического коефициентов переноса а также количества электронов включенных в реакцию определящую скорость и кроме того и формальный стандартный потенциал системы. Этот метод значительно просче, чем хорошо известный метод Геришера-Филштыха и особенно имеет преимущество, когда R высокореактивное соединение или вид амалгамы неустойчивой на воздухе. Верхний предел k_s, который может быть определен с помощью описаного метода соответствует результатам полученым методом Геришера-Филштыха. Кинетические параметры найденные данным методом для электродных реакции цинк-ион/цинк-амалгама в IM азотнокислом калии, медь /2+/ион-медьная амалгама в том же самом растворе и кадмий/ион-кацмиевая амалгама в 0,5м сульфате хорошо соответствуют данным известным из литературы.

The boron-carbon-hydrogen system: I. SHAPIRO, *Talanta*, 1964, **11**, 211. (Universal Chemical Systems, Inc., Culver City, California, U.S.A.)

Summary—Identification of many newly-discovered compounds composed only of the three elements, B, C and H, has been accomplished by use of mass, infrared and nuclear magnetic resonance spectroscopy in conjunction with the isotopic substitution technique. These compounds can be classified into two general categories: (1) the organo derivatives of boron hydrides, and (2) the carboranes (and their organo derivatives). Examples of compounds identified by purely spectroscopic means are given.

Polarographic reduction of manganese^{III} in an alkaline tartrate solution: N. TANAKA, Y. KIKUCHI and Y. SATO, *Talanta*, 1964, **11**, 221. (Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan.)

Summary—The formation of manganese^{III} complexes by the air oxidation of manganese^{II} in alkaline tartrate solution is confirmed by measurement of the direct current and the Kalousek polarograms. A distinct minimum is observed on the polarogram in the pH range from 10 to 13. The effects of pH, the concentration of sodium tartrate and surface-active substances on the polarogram are investigated, and the electrode processes of manganese^{III} in an alkaline tartrate solution are discussed.

A modification of the exponential exchange law is heterogeneous systems: B. VAN'T RIET and L. J. PARCELL, *Talanta*, 1964, **11**, 231. (Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia, U.S.A.)

Summary—The exponential exchange law for heterogeneous systems can be applied to isotope exchange between solid salts and their saturated solutions after allowance is made for the initial rapid exchange between the solution and the crystal surface. For a variety of salts it is possible to get information on the dynamic equilibrium between the surface and the interior of the crystals. Experimental results are presented for the chromates of silver, barium and lead. Silver chromate exchanges rapidly with silver ion, without showing significant exchange with chromate ion. Recrystallisation effects are evident in the chromates of barium and lead.

СИСТЕМЕ БОР-УГЛЕРОД-ВОДОРОД:

I. Shapiro, *Talanta*, 1964, **11**, 211.

Резюме—Была проведена идентификация многих новых соединений состоящих только из 3 элементов B, C, и H, при помощи масс-, инфракрасной спектроскопии и спектроскопии ядерных магнетических резонансов в связы с техникой изотопной субституции. Эти соединения могут быть классифицированы на 2 основные категории:

(1) органические производные от гидридов бора

(2) соединения бора с углеродом (и их органические производные)

Приводятся примеры соединений идентифицированных только при помощи спектроскопии.

ПОЛЯРОГРАФИЧЕСКОЕ ВОССТАНОВЛЕНИЕ МАРГАНЦА В РАСТВОРАХ ШЕЛОЧНЫХ ТАРТАРАТОВ:

Nobuyuki Tanaka, Yasuko Kikuchi and Yuichi Sato, *Talanta*, 1964, **11**, 221.

Резюме—Исследовалось образование комплексов трехвалентного марганца при окислении воздухом двухвалентного марганца в щелочном растворе тартарата при помощи измерения непосредственого тока и из полиярограммов типа Калоуска. Отчетливый минимум наблюдался на полярографических кривых в области pH 10–13. Исследовалось влияние pH, концентрации тартарата натрия и поверхностно активных веществ на кривие. Обсуждаются электродные процессы трехвалентного марганца в щелочном растворе тартарата.

МОДИФИКАЦИЯ ЗАКОНА ЭКСПОНЕНЦИАЛЬНОГО ОБМЕНА В НЕОДНОРОДНЫХ СИСТЕМАХ:

B. van't Riet and L. J. Parcell, *Talanta*, 1964, **11**, 231.

Резюме—Закон експоненциального обмена для гетерогенных систем может быть приложен к изотопному обмену между твердыми солями и их насыщенным раствором при учитывании начальной скорости обмена между раствором и кристалической поверхностью. Для различных солей возможно получить информации о динамическом равновесии между поверхностью и внутренней частью кристаллов. Экспериментальные данные приводятся для хроматов серебра, бария и свинца. Хромат серебра быстро обменивается с ионами серебра, причём обмен с ионом хромата не происходит. Эффект рекристализации очевидный у хромата бария и свинца.

Reaction of iron^{III} with hydroxyaminoacids: ***N,N*-Dihydroxyethylglycineiron^{III}:** E. R. NIGHTINGALE, JR. and R. F. BENCK, *Talanta*, 1964, **11**, 241 (Esso Research and Engineering Company, P.O. Box 121, Linden, N.J., U.S.A.)

Summary—The stoichiometry and equilibrium for the reaction of iron^{III} with *N,N*-dihydroxyethylglycine in aqueous medium has been investigated. Iron^{III} is shown to form only a 1:1 complex with the ligand; previous reports of a 2:3 complex are demonstrated to be erroneous, and probably resulted from non-equilibrium titration measurements. Using a modified Bjerrum titration procedure, the equilibrium constant for the formation of the 1:1 complex at 25° has been determined to be $3{\cdot}8 \times 10^{-8}$ moles^2/litre^2. Attempts to differentiate between alternative structures for the complex are inconsequential, because the complex exists only in aqueous medium, where the ligand hydroxyl groups exchange rapidly with solvent water.

Potentiometric study of the complexes of mercury^{I} with pyrophosphate, triphosphate and tetraphosphate: JAMES I. WATTERS and RICHARD A. SIMONAITIS, *Talanta*, 1964. **11**, 247. (Macpherson Chemical Laboratory, The Ohio State University, Columbus 10, Ohio, U.S.A.)

Summary—The dimer of mercury^{I} forms stable complexes with polyphosphates. The stabilities of these complexes decrease slightly as the chain length increases. Because of the strong tendency of mercury^{I} to associate with hydroxide ions, the mixed complex species containing both polyphosphate and hydroxide ions were found to be the predominant species in slightly alkaline solutions. In polyphosphate solutions, polarographic waves of Hg^{I} and Hg^{II} are obtained at similar potentials, because the Hg^{II} reacts chemically with the mercury of the drop to form Hg^{I} complexes before the electrode reaction occurs. Similar anodic waves are obtained in the presence or absence of mercury ions in solution because of the formation of mercury^{I} complexes. The tetraphosphate complexes which have not been studied before, and their over-all complexity constants in the presence of 1*M* KNO_3 and 0·15*M* guanidinium ion at 25°, are:

$Hg_2(P_4O_{13})^{4-}$, $10^{7{\cdot}32}$; $Hg_2(P_4O_{13})_2^{10-}$, $10^{9{\cdot}88}$;

$Hg_2(P_4O_{13})(OH)^{5-}$, $10^{15{\cdot}26}$; $Hg_2(P_4O_{13})(OH)_2^{6-}$, $10^{22{\cdot}45}$.

РЕАКЦИЯ ЖЕЛЕЗА (III) С ГИДРОКСИАМИНОКИСЛОТАМИ. N,N-ДИГИДРОКСИЭТИЛГЛИЦИНЖЕЛЕЗО (III): E. R. NIGHTINGALE, JR. and R. F. BENCK, *Talanta*, 1964, **11**, 241.

Резюме—Исследовалось стехиометрия и равновесие реакции Fe(III) с N,N′-дигидроксиэтилглицином в водной среде. Было показано, что Fe(III) образует с последним только комплекс I:I. Было показано, что комплекс 2:3 о котором сообщалось ранее выл ошибочным и явился вероятно результатом измерений неравновесного титрования. Используя модифицированный метод титрования Биерума, была определена константа образования комплекса I:I при 25°C равная 3,8 . 10 моль^2/л^2. Структура комплекса не была точно определена, т.к. комплекс существует только в водной среде, где гидроксильные группы N,N′-дигидроксиэтиленглицина быстро обмениваются с растворителем.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ КОМПЛЕКСОВ РТУТИ (I) С ПИРОФОСФАТАМИ ТРИФОСФАТАМИ И ТЕТРАФОСФАТАМИ: JAMES I. WATTERS and RICHARD A. SIMONAITIS, *Talanta*, 1964, **11**, 247.

Резюме—Димер ртути образует устойчивые комплексы с полыфосфатами. Устойчивость этих комплексов слегка понижается с увеличением длины цепя. Было определено, что в слабощелочных растворах преобладают смешанные комплексы содержащие полыфосфатные и гидроксоионы. Полярографические волны одно и двухвалентной ртути в полыфосфатных растворах находятся при близких потенциалах, так как Hg/2+ /реагирует со ртутью капельного электрода образуя Hg/I$_+$/комплексы прежде чем протекает электродная реакция. Похожие анодические волны были получены в присутствии и отсутствии ионов ртути в растворе, обусловленые образованием комплексов одновалентной ртути. Константы устойчивости до сих пор неизученых тетрафосфатных комплексов в присутствии IM KNO_3 и 0,15M гванидина при 25°C:

$$Hg_2/P_4O_{13}/^{4-},\ 10^{7,32};\ Hg_2/P_4O_{13}/_2^{10-},\ 10^{9,88};$$

$$Hg_2/P_4O_{13}/\quad /OH/^{5-},\ 10^{15,26};\ Hg_2/P_4O_{13}/\quad /OH/_2^{6-},\ 10^{22,45}.$$

Analytical applications of radioactive vitamin B_{12}: C. ROSENBLUM, *Talanta*, 1964, **11**, 255. (Merck Sharp and Dohme Research Laboratories, Division of Merck and Co., Inc., Rahway, New Jersey, U.S.A.)

Summary—Radioactive vitamin B_{12} has been employed as an analytical tool, a biochemical tracer and as a diagnostic agent. Of the several labelled modifications reported, only those labelled with cobalt isotopes are useful at physiological dose levels. Because of the high specific activities of (1–200) $\mu c/\mu g$, detection sensitivities in the picagram region are realised with cobalt-labelled vitamin B_{12}. Clinical applications including diagnostic tests for pernicious anaemia in humans, are in a sense analytical procedures, involving as they do measurements of vitamin B_{12} transport. Of more direct analytical character is the application of the isotope dilution method to pharmaceutical preparations, feed concentrates, sewage and fermentation products and crystalline cobalamins. The stability of hydroxocobalamin in pH 4·2 stabilised aqueous solution has been demonstrated by this method. The reverse isotope dilution method also has been very helpful in facilitating stability and degradation studies. The quantitative recovery of unchanged cyanocobalamin from cereals and from capsules containing biological concentrates has been demonstrated by this method. By contrast, the conversion of cyanocobalamin to hydroxocobalamin has been found to occur in the liver of dogs receiving labelled vitamin. An extensive study of protective agents to stabilise vitamin B_{12} in solutions containing ascorbic acid has been performed by this reverse dilution procedure. The sensitivity of the isotope dilution method has been greatly extended to physiological levels by the application of "saturation analysis," an extension of the binding power measurement applied to intrinsic factor concentrates and to animal tissues including serum or plasma.

Some physical properties of highly purified bromine: M. S. CHAO and V. A. STENGER, *Talanta*, 1964, **11**, 271. (Special Services Laboratory; The Dow Chemical Company, Midland, Michigan, U.S.A.)

Summary—The electrical conductivity of very pure bromine is lower than that given in most of the earlier literature, and the surface tension is slightly higher. In the liquid range, these properties can be expressed by the equations $\log k = -11{\cdot}372 + 0{\cdot}0128t$ and $\gamma = 45{\cdot}5 - 0{\cdot}182$, where k is in $ohm^{-1}.cm^{-1}$, γ in $dyne.cm^{-1}$ and t in °C. Data on the thermal conductivity of the liquid are given for the first time.

АНАЛИТИЧЕСКОЕ ПРИМЕНЕНИЕ РАДИАКТИВНОГО ВИТЕМИН B_{12}: C. Rosenblum, *Talanta*, 1964, **11**, 255.

Резюме—Радиоактивный витамин B_{12} был использован в качестве аналитического реагента, биохимического метчика а так же в качестве диагностического агента. Среди многих известных меченых соединений только соединения меченые изотопами кобальта могут быть использованы в количествах соответствуюущих физиологическим дозам. Благодаря высокой уделной активности /1–200$\mu c/\mu g$/ чувствительность определения достигает порядком 10^{-12} г. при помощи витамина B_{12} меченного кобальтом. Клиническое использование включая диагностические тесты перникулозной анемии человека, проводится с помощю измерения транспорта витамина B_{12} в организме. Характер непосредственного анализа имеет метод изотопного разбавления в фармацевтии, в концентрировании продуктов, в анализе отбросных вод, продуктов ферментации а кристалических кобаламинов. Устойчивость гидроксокобаламина в стабилизированном водном растворе /pH 4,2/ было показано при помощи этого метода. Метод обратного изотопного разбавления может быть широко использован в исследовании стабильности и при изучении деградации. С помощью этого метода было проведено количественное определение не измененного цианокобаламина в злаках и других биологических материалах. Наоборот, в печени собак получающих меченый витамин было найдено превращение цианоцобаламина в гидроксикобаламин. При помощи обратного изотопного разбавления было проведено изучение защищающих агентов для стабилизации витамина B_{12} в растворах содержащих аскорбиновую кислоту. Метод изотопного разбавления находит широкое применение в физиологии особенно для своей высокой чувствительности.

НЕКОТОРЫЕ ФИЗИЧЕСКИЕ СВОЙСТВ ОЧИЩЕНОГО БРОМА: M. S. Chao and V. A. Stenger, *Talanta*, 1964, **11**, 271.

Резюме—Было показано, что электропроводность очень чистого брома ниже чем электропроводность описанная ранее в литературе а поверхностные силы немного выше. В текучей области эти свойства могут быть выражены уравнениями: $\log \kappa = -11.372 + 0{,}0128t$ и $\gamma = 45{,}5-0{,}182t$, где к выражено в ом/цм, γ в дин/цм и t в °C. Данные термопроводности жидкости приводятся впервые.

D_2O effect on $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in the iron^{II}–iron^{III} electron-exchange reaction: Shouzow Fukushima and Warren L. Reynolds, *Talanta*, 1964, **11,** 283. (Chemistry Department, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.)

Summary—The equilibrium constant of the reaction $Fe^{3+} + D_2O \rightarrow FeOD^{2+} + D^+$ has been measured at 0·500 ionic strength at 5°, 15° and 25°. The ΔH and ΔS of this reaction are $9{\cdot}32 \pm 0{\cdot}56$ kcal.mole^{-1} and $17{\cdot}7 \pm 2{\cdot}0$ cal. deg.$^{-1}$ mole^{-1}, respectively. The rates of the electron-exchange reactions $Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+}$ and $Fe^{2+} + {}^*FeOD^{2+} \rightarrow FeOD^{2+} + {}^*Fe^{2+}$ have been measured at 0·500 ionic strength at 5°, 15° and 25°. The enthalpy and entropy of the latter reaction are $11{\cdot}5 \pm 0{\cdot}5$ kcal. mole^{-1} and $-4{\cdot}0 \pm 1{\cdot}8$ cal. deg.$^{-1}$ mole^{-1}, respectively.

Lead-dithizone equilibria in water-carbon tetrachloride systems: O. B. Mathre and E. B. Sandell, *Talanta*, 1964, **11,** 295. (School of Chemistry, University of Minnesota, Minneapolis, Minnesota, U.S.A.)

Summary—Equilibrium of the principal reactions involved in the extraction of lead dithizonate from aqueous solution with carbon tetrachloride (0) have been determined at $\mu = 0{\cdot}1$:

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{2+}][H_2Dz]_0{}^2} = 5{\cdot}6 \pm 0{\cdot}3 \qquad (5{\cdot}8 \pm 0{\cdot}6 \text{ at } \mu = 0{\cdot}3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{soly. in } CCl_4}{\text{soly. in } H_2O} = \frac{6 \times 10^{-6}}{3 \times 10^{-9}} = 2 \times 10^3$$

$$K_{diss} = \frac{[Pb^{2+}]HDz^-]^2}{[Pb(HDz)_2]} = 7 \times 10^{-16}$$

$$K_{sp} = [Pb^{2+}][HDz^-]^2 = 2 \times 10^{-24} \qquad \frac{[HPbO_2{}^-](aH^+)^3}{[Pb^{2+}]} = 7 \times 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{2+}][Cit^{3-}]} = 5{\cdot}4 \times 10^5 \qquad \frac{[PbNO_3{}^+]}{[Pb^{2+}][NO_3{}^-]} = 0{\cdot}11$$

The pH range for extraction of >99% of lead under analytical conditions (citrate and cyanide present, low equilibrium concentration of dithizone) is 7·5–11·5. Cyanide in the concentrations likely to be used does not significantly decrease the extraction of lead. Above pH 10·85, >99% of the excess dithizone is extracted from the carbon tetrachloride phase into an equal volume of aqueous phase. A pH of 10·8–10·9 is recommended for determination of lead with a carbon tetrachloride solution of dithizone. A variation of *ca.* ~0·2 pH unit from this value causes little error.

D_2O ЭФФЕКТ НА $\Delta H^{\ddagger}$ И $\Delta S^{\ddagger}$ ПРИ ОБМЕННОЙ ЭЛЕКТРОДНОЙ РЕАКЦИИ: Fe(II) + Fe(III): SHOUZOW FUKUSHIMA and WARREN L. REYNOLDS, *Talanta*, 1964, **11**, 283.

Резюме—Были измерены константы равновесии реакции $Fe^{3+} + D_2O \rightarrow FeOD^{2+} + D^+$ при 0,500 ионой силе (при 5°, 15° и 25°C). Для ΔH и ΔS были найдены величниы $9{,}32 \pm 0{,}56$ килокал.мол$^{-1}$ и $17{,}7 \pm 2{,}0$ кал.град.$^{-1}$ мол$^{-1}$ соответственно. Скорости обмена электронов в реакциях $Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+}$ и $Fe^{2+} + {}^*FeOD^{2+} \rightarrow FeOD^{2+} + {}^*Fe^{2+}$ измерались при ионой силе 0,500 и 5°, 15° и 25°C. Энтальпия и энтропия активации выше упомянутых реакции была $11{,}5 \pm 0{,}5$ килокал. мол$^{-1}$ и $-4{,}0 \pm 1{,}8$ кал.град$^{-1}$ мол$^{-1}$ соответственно.

РАВНОВЕСИЯ ДИТИЗОНАТА СВИНЦА В СИСТЕМЕ ВОА- ЧЕТЫРЕХЛОРИСТЫЙ УГЛЕРОД: O. B. MATHRE and F. B. SANDELL, *Talanta*, 1964, **11**, 295.

Резюме—Изучались константы равновесия основных реакций экстракции дитизоната свинца тетрахлористым углеродом. При $\mu = 0{,}1$:

$$K_{\text{экс}} = \frac{[Pb/HDz/_2]_0/aH^+/^2}{[Pb^{2+}][H_2Dz]_0^2} = 5{,}6 \pm 0{,}3\ /5{,}8 \pm 0{,}6 \text{ при } \mu = 0{,}3/$$

$$P = \frac{[Pb/HDz/_2]_0}{[Pb/HDz/_2]} = \frac{\text{раств. } CCl_4}{\text{раств. } H_2O} = \frac{6 \times 10^{-6}}{3 \times 10^{-9}} = 2 \times 10^3$$

$$K_{\text{дисс}} = \frac{[Pb^{2+}][HDz^-]^2}{[Pb/HDz/_2]} = 7 \times 10^{-16}$$

$$K_{\text{сп}} = [Pb^{2+}][HDz^-]^2 = 2 \times 10^{-24} \qquad \frac{HPbO_2^-]/aH^+/^3}{[Pb^{2+}]} = 7 \times 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{2+}][Cit^{3-}]} = 5{,}4 \times 10^5 \qquad \frac{[PbNO_3^+]}{[Pb^{2+}][NO_3^-]} = 0{,}11$$

В области pH между 7,5–11,5 экстракция свинца более 99% в аналитических условиях /присутствие цитрата и цианата, низкая равновесная концентрация дитизона/. Цианид в обычно используемой концентрации неснижает экстракцию свинца. При pH более 10,85 99% избытка дитизона экстрагируется из органической фази в равный объем водной фази. Область pH 10,8–10,9 рекомендуется для определения свинца раствором дитизона в тетрахлориде углерода. При отклонении pH ~0,2 pH возникает небольшая ошибка.

The anodic amperometric titration of low concentrations of nitrite with sulphamic acid or cerium^{IV} ion: J. T. Stock and R. G. Bjork, *Talanta*, 1964, **11**, 315. (Department of Chemistry, University of Connecticut, Storrs, Connecticut, U.S.A.)

Summary—Nitrite at a concentration of approximately $6 \times 10^{-4}M$ in 0·05*M* sulphuric acid can be titrated amperometrically at a rotating platinum micro-anode with sulphamic acid or cerium^{IV} ion. Results with sulphamic acid are free from bias and have a standard deviation of about 1%. Titration with cerium^{IV} is less precise, giving results that are high or low according to the method used for end-point location, but is applicable to lower nitrite concentrations than is titration with sulphamic acid.

Effects of adsorbed films of camphor and thymol on kinetics of the titanium^{IV}–titanium^{III} electrode reaction: H. A. Laitinen, K. Eda and M. Nakanishi, *Talanta*, 1964, **11**, 321. (Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, U.S.A.)

Summary—The effect of contamination of a mercury surface by camphor and thymol on the standard rate constant of the titanium^{IV}–titanium^{III} half reaction in 1*M* tartaric acid has been determined by means of voltage-step and impedance methods. Complications arising from specific adsorption of the electronegative species proved more disturbing to the impedance method than to the voltage-step method. A linear decrease of rate constant with surface coverage is indicated.

Chronopotentiometric study of thallous ion in glacial acetic acid: S. Bruckenstein, T. O. Rouse and Stephen Prager, *Talanta*, 1964, **11**, 337. (Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, U.S.A.)

Summary—The thallous ion-thallium amalgam system has been studied chronopotentiometrically in glacial acetic acid (HAc) as a solvent, using 0·25*M* ammonium acetate as supporting electrolyte. The transition time relationships between the cathodic transition time and the first anodic transition time on current reversal were verified. Analogous studies were carried out at the thallium amalgam electrode, determining the anodic transition time and the cathodic transition time on current reversal. The predicted potential-time relationships for the above-mentioned chronopotentiometric processes were verified, and it was established that the thallous acetate-thallium amalgam couple is reversible with the formal potential of 0·347 ± 0·005 V *vs.* the saturated aqueous calomel electrode. The diffusion coefficients of thallous ion and thallium in mercury were found to be identical, $4{\cdot}3 \times 10^{-6}$ cm^2. sec^{-1}.

Summaries for card indexes

АНОДИЧЕСКОЕ АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ НИЗКИХ КОНЦЕНТРАЦИЙ НИТРИТОВ ПРИ ПОМОЩИ СУЛЬФАМОВОЙ КИСЛОТЫ: J. T. Stock and R. G. Bjork, *Talanta*, 1964, **11**, 315.

Резюме—Было показано, что нитрит в концентрации приблизительно 6×10^{-4} M в 0,05M серной кислоте можно титровать амперометрически при помощи вращающейся платиновой микроаноды с сульфоамидовой кислотой или четырехвалентным церием. Результаты с сульфоамидовой кислотой точнее с ошибкой около 1%. Определение титрированием Ce^{4+} менее точное так как результаты или высокие или низкие в зависимости от метода определения конца титрирования. Титрирование четырехвалентным церием удобнее для более низких концентраций нитрита чем титрование сульфамиловой кислотой.

ВЛИЯНИЕ АДСОРБИРОВАННЫХ КАМФОРА И ТИМОЛА НА ЭЛЕКТРОДНУЮ РЕАКЦИЮ ТИТАНА(4)-ТИТАНА(3): H. A. Laitinen, K. Eda and M. Nakanishi, *Talanta* 1964, **11**, 321,

Резюме—Эффект загрязнения поверхности ртути камфором и тимолом на стандартную константу скорости полуреакции титан(IV)-титан(III) в 1M винной кислоте был определен с методами ступенчатого напряжения и импеданса. Оказалось что осложнения в следствии специфической адсорбции электроактивного рода имеют больше влияния на метод импенданса, чем на метод ступенчатого напряжения. Указано линейное понижение константы скорости с покритием поверхности.

ХРОНОПОТЕНЦИОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ ОДНОВАЛЕНТНОГО ТАЛЛИЯ В ЛЕДЯНОЙ УКСУСНОЙ КИСЛОТЕ: S. Bruckenstein, T. O. Rouse and Stephen Prager, *Talanta*, 1964, **11**, 337.

Резюме—Система ион таллия(I)-амальгама таллия была исследована хронопотенциометрическим методом в ледяной уксусной кислоте (HAc) как растворителем, с 0.25 M раствором уксуснокислого аммония как поддерживающим электролитом. Проберены отношения между катодным временем перехода и первым анодым временем перехода при перемене направления тока. Одинаковые исследования были проведены на электроде амальгамы таллия, определяя анодное и катодное время перехода при перемене направления тока. Были проверены предсказанные отношения между потенциялом и временем за спомянутые хронопотенциометрические процессы и было утверждено что пара ацетат таллия(I)-амальгама таллия обратима с формальным потенциялом 0.347 ± 0.005 V в отношении к насищенном каломельевом електроде. Коэфициенты диффузии иона таллия(I) и таллия в ртути показались одинаковыми—4.3×10^{-6} см^2/сек.

Radiochemical determination of strontium-89 and -90 in uranium minerals and salts: P. K. KURODA and H. ARINO, *Talanta*, 1964, **11**, 343. (Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A.)

Summary—A combination of low-level counting technique and large-scale analytical operation has been employed to determine extremely small quantities of strontium-89 and -90 in uranium ores and salts. Strontium carrier is added to a kilogram quantity of the samples of non-irradiated uranium ore and salt, exhaustively purified, and counted. The levels of radiostrontium found are of the order of 10^{-4} disintegrations.$sec^{-1}.g^{-1}$ of uranium in the sample. These strontium isotopes are formed in non-irradiated uranium salts and ores predominantly by the spontaneous fission of uranium, but neutron-induced fission of uranium-235 also appears to occur in the latter.

Publications of Izaak Morits Kolthoff: *Talanta*, 1964, **11**, 351.

РАДИОХИМИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СТРОНЦИЯ 89 И 90 В СОЛЯХ И МИНЕРАЛАХ УРАНА: P. K. KURODA and HIROFUMI ARINO, *Talanta*, 1964, **11**, 343.

Резюме—Был разработан метод определения исключительно малых количеств стронция-89 и 90 в урановых рудах и солях. С помощью техники счета очень низких активностей и обработки макрообразцов. Носитель для стронция добавлялся к килограммовым количествам образцов необлученых солей или руд урана, тщательно очищен и его активность измерена. Количества радиоактивного стронция были порядком 10^{-4} распадов/сек/грамм урана в образце. Изотопы стронция образуются в солях и рудах урана главным образом при спонтанном распаде урана.

РАБОТЫ ИЗАКА МОРИЦЕ КОЛЬТГОФА: *Talanta*, 1964, **11**, 351.

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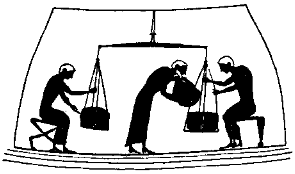

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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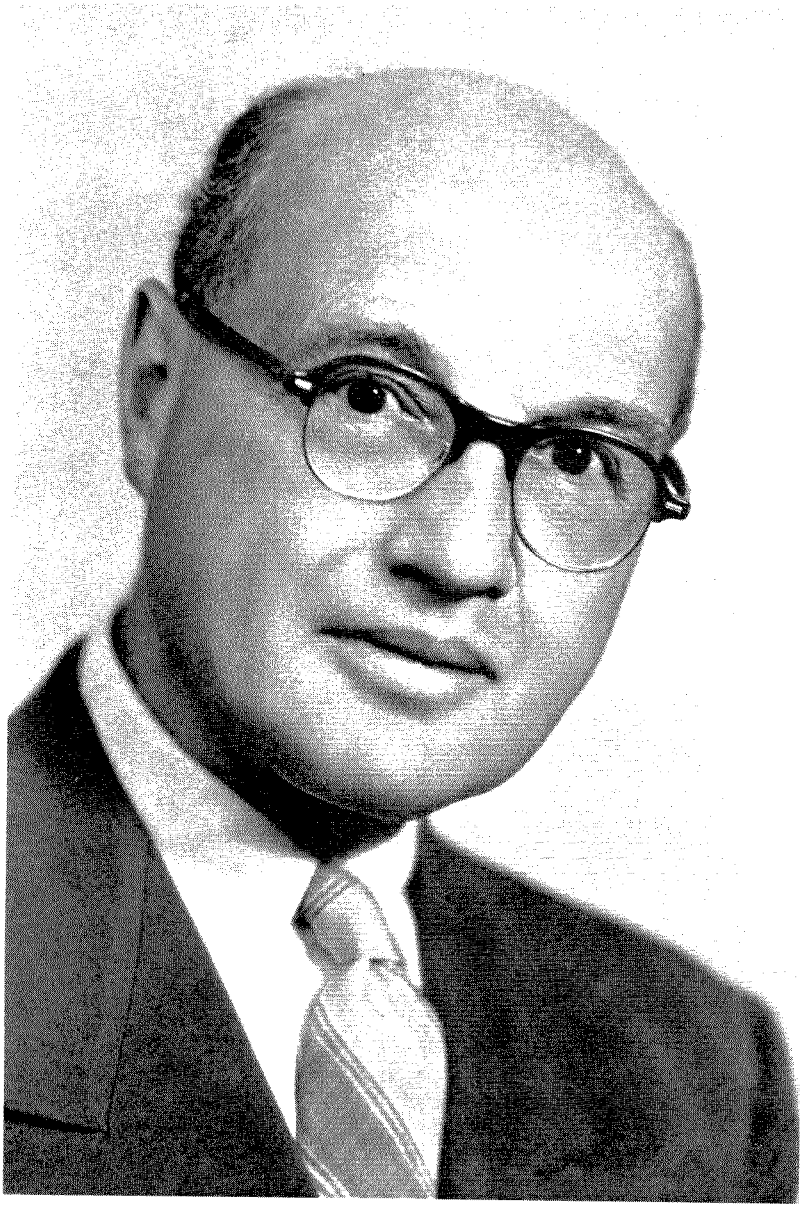
EDITOR'S FOREWORD

THE Editorial Board and Publishers of TALANTA take pleasure in honouring the seventieth year of

IZAAK MAURITS KOLTHOFF

by presenting this special issue, which is comprised entirely of invited contributions from his former students and associates.



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IZAAK MAURITS KOLTHOFF

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Department of Chemistry, Harvard University, Cambridge 38, Mass., U.S.A.

IZAAK MAURITS KOLTHOFF, son of Moses and Rosetta (Wysenbeck) Kolthoff, was born on February 11, 1894, in Almelo, Holland.

In 1911, after graduation from Hoogereburger School, young Kolthoff's interest in chemistry already had been aroused, and the next logical step would have been graduate study of chemistry in a university. However, although he was fluent in English, French and German, in addition to his native Dutch, Kolthoff was barred from academic work in the "pure" physical sciences because he lacked the knowledge of Latin and Greek which at that time was a pre-requisite. As an alternative he enrolled in the chemical engineering curriculum at the University of Delft, but only a fortnight's stay convinced him that his real interest was elsewhere. Accordingly, he transferred to the school of pharmacy at the University of Utrecht. Here he came under the tutelage of Professor Nicholas Schoorl who guided him into his true vocation in analytical chemistry.

In retrospect, it might be said that one of the most important circumstances that has shaped the development of analytical chemistry over the past fifty years was Kolthoff's failure to acquire a knowledge of Latin and Greek during his high school days! If he had done so he probably would have gone on in the usual way to a university course in the "pure" physical sciences, he would not have come under the influence of Professor Schoorl, and, more than likely, analytical chemistry of our time would have been deprived of one of its most influential architects.

Kolthoff's first diploma at Utrecht was that of "Pharmacist", but the six-year curriculum on which it was based actually provided an education in chemistry as good as any available at that time. Indeed, the education in analytical chemistry offered by Professor Schoorl would have been hard to match anywhere, because Schoorl employed the approach (then rare) of emphasising the fundamental science underlying analytical chemistry and also had the gift of being able to inculcate in his students an appreciation for the equally important factual aspects of the subject. Schoorl's motto "Theory guides; experiment decides." has been the cardinal guiding principle of Kolthoff's scientific life.

In 1918, following an enlightened change in Dutch academic laws pertaining to the role of the classical languages in science education, Kolthoff was awarded the Ph.D. degree in chemistry from Utrecht for a thesis entitled *Fundamentals of Iodimetry*. This was not his first piece of original scientific investigation; actually, he had published his first research paper in 1915, and by 1918 it had been joined by 32 more papers all on subjects different from his Ph.D. thesis. His Ph.D. thesis itself certainly was not "thin", when one considers the series of nineteen papers on iodometric methods based on it which he published during 1919 and 1920. All this by the age of 26!

Dr. Kolthoff served as Conservator of the Pharmaceutical Institute at the University of Utrecht from 1917 to 1927, and concurrently as *privat docent* in applied electrochemistry from 1924 to 1927. Apparently a *privat docent* at that time was one who worked very hard in a university as teacher and investigator without being distracted by a salary! That this arrangement was well suited to Kolthoff's love of original investigation is evident from the fact that during this brief ten-year period he published 270 more research papers and wrote three books.

By 1927 not merely the amazing volume of his publications, but rather their high degree of originality and importance in analytical chemistry, had earned for Dr. Kolthoff an international reputation and he was invited on a lecture tour to Canada and the United States. Following this tour he accepted the position of Professor and Chief of the Division of Analytical Chemistry at the University of Minnesota. During the next 35 years, under his influence, the University of Minnesota became renowned as a leading research centre in analytical chemistry. In June 1962 Professor Kolthoff "retired", but for him this word is meaningless and his contributions to analytical chemistry continue unabated.

Kolthoff began his scientific life at the time when analytical chemistry was just emerging from its age of empiricism, and when applications of the principles of physical chemistry to analytical problems were appreciated only vaguely, and even vaguely by only a few. When he took his first course in quantitative analysis in 1913, S. P. L. Sörensen's definition of pH was only four years old, and even Arrhenius' theory of electrolytic dissociation was still a novel idea. Kolthoff began to demonstrate how these then new principles of solution physical chemistry could be applied to interpret, rationalise, and improve titrimetric analytical methods.

His earliest studies were in the field of acid-base titrimetry, and, beginning about 1914, he instituted a series of investigations of the dissociation equilibria of various weak acids and bases, the functional mechanism and characteristics of acid-base indicators, the use of indicators and indicator test-papers for pH measurement, and the properties of standard buffer solutions. He not only carried out studies in this field which were truly fundamental, but he also applied the knowledge thus gained to the development of many practical procedures. This combination of fundamental theory and practical application has been a characteristic of all his work ever since. These studies led to the publication in 1922 of his first monograph *Der Gebrauch von Farbenindicatoren.* That this book satisfied a real need is shown by the fact that it went through four editions between 1922 and 1932, and was translated into English by N. Howell Furman in 1926. In 1932 in collaboration with Harry Fischgold it was revised as *Säure-Basen Indicatoren,* and in 1937, with the assistance of Charles Rosenblum, it was again revised as *Acid-Base Indicators.*

Electrometric methods of analysis owe much of their development to Kolthoff, who appreciated their potentialities and began to exploit them when they were still virtually unknown to most analytical chemists. Starting about 1918 he carried out many studies of the application of electrolytic conductance to end-point detection in titrations, and these culminated in the appearance of his second monograph, *Konduktometrische Titrationen,* in 1923. This book was one of the first to systematise the theory and applications of the conductometric method. It also illustrates another of Kolthoff's characteristic traits, namely, that whenever he devotes himself to a particular subject a good monograph soon appears!

Another subject pioneered by Kolthoff was the field of potentiometric measurements and titrations. In connection with his investigations of protolytic equilibria and pH measurements he published many papers on the hydrogen, quinhydrone, antimony and other pH electrodes. Characteristically, these were particularly valuable because they emphasised the limitations and sources of error of the then relatively new potentiometric method of pH measurement. Kolthoff's approach to analytical problems *via* fundamental theory proved especially fruitful in his many studies of potentiometric equivalence-point detection in precipitation, complexation and redox titrations. In 1926, in collaboration with N. Howell Furman, Kolthoff published *Potentiometric Titrations*, the first monograph on this subject published in the United States. A second revised edition appeared in 1931, and even after 30 years it is still a most useful source of information on the practical performance of potentiometric titrations and on actual procedures.

The studies cited above, which engaged Kolthoff's attention during the period from 1915 to about 1926, would have been more than sufficient to satiate the scholarly impulses of any ordinary scientist. But during this same decade he had also found time to cultivate many other aspects of classical titrimetric analysis, and he recognised the need for a treatise on titrimetric analysis which would provide a comprehensive treatment of the theory of the subject and a critical evaluation and description of its manifold specific applications. Accordingly in 1927, with H. Menzel, he published the first volume of his famous *Massanalyse* (*Die theoretischen Grundlagen der Massanalyse*), and a year later this was followed by the second volume *Die Praxis der Massanalyse.* In 1928 the first American edition under the title *Volumetric Analysis* was made available with the translational assistance of N. Howell Furman. Kolthoff did not merely edit this book; he created it by personally testing nearly every procedure which it contained. During the period from 1942 to 1957 a revised edition was published in three volumes with the co-authorship of Vernon A. Stenger, George Matsuyama and R. Belcher, and it stands today as the most authoritative monograph on its subject.

Influenced by the great Dutch chemist H. R. Kruyt, Kolthoff had early acquired an interest in colloidal phenomena and surface chemistry. When he came to Minnesota in 1927 he intensified the investigations on coprecipitation and adsorption by precipitates which he had begun in Holland. He directed these studies to such analytically important precipitates as those of the Hydrogen Sulphide and Ammonia Groups, calcium oxalate, barium sulphate and the silver halides. The results obtained have done much to rationalise the practice of gravimetric analysis, and have added very significantly to knowledge of the mechanisms involved in the formation of micro-crystalline precipitates, and to the behavioural mechanism of adsorption indicators. In these studies Kolthoff, in collaboration with Charles Rosenblum, was among the pioneers in the use of radioactive indicators (Th B for Pb). At that time (1930) only the natural radioactive isotopes were available, and the activity was measured with a gold leaf electroscope.

During the fall of 1934 Kolthoff's interest was again attracted to electometric analysis, this time to polarographic analysis with the dropping mercury electrode. Polarography had been invented about a decade previously by Jaroslav Heyrovský at the Charles University in Prague, and the reader will recall that this discovery was rewarded recently by the award of the Nobel Prize in Chemistry to Professor Heyrovský. Although European analytical chemists had been quick to realise its potentialities, polarography was still unknown in the United States in the middle

1930's. Approaching this subject in characteristic fashion, Kolthoff's first concern was the theoretical basis of the method, and he carried out important studies of the various factors which influence the diffusion current, polarographic maxima, and the current-potential inter-relationship. At this same time, in collaboration with Herbert A. Laitinen, he instituted a series of studies on polarographic (voltammetric) analysis with stationary and rotated platinum microelectrodes. He was quick to recognise the potential utility of amperometric titration, and he played a major role in bringing this method to its present well-developed state. It was quite in character that he was not content merely to contribute to polarographic analysis by his own investigations. Realising the need for correlation and systematisation he published in 1941, with this writer's assistance, the monograph *Polarography*. This was the first comprehensive and critical treatment of the subject in the English language and it was a potent factor in the accelerated development of polarographic analysis which began in the early 1940's. A second, much enlarged edition of *Polarography* in two volumes appeared in 1952, and Professor Kolthoff currently is busy with the preparation of a third edition.

With the advent of the war in 1942, Kolthoff forsook his academic interests to direct a research project for the Office of Rubber Reserve. From pure analytical chemistry to synthetic rubber did not entail as drastic a change in Kolthoff's activities as might be supposed. The acquisition of detailed knowledge of the kinetics of polymerisation reactions in solution was an essential part of this programme, and, because the experimental study of such kinetics depends primarily on analysis, Kolthoff was eminently qualified for this task.

After the war Kolthoff again picked up the many irons which he had had to let cool by the fire's edge, although several years passed before the odour of styrene finally disappeared from the atmosphere of his laboratory. (As recently as 1957 he was still publishing results of his studies of the emulsion polymerisation of styrene.) He returned to his studies of polarography and amperometric titrations, and a steady stream of communications from his laboratory continues to enrich this field.

A complete list of Kolthoff's research publications up to about the end of 1963 is appended (p. 351). This list is restricted to original research papers, and it does not include routine writings such as book reviews, *etc.* No attempt will be made here to analyse in detail the amazing volume and variety of these contributions. The reader will appreciate that to do so adequately would require a book-length discussion, and I leave this task to some future historian of analytical chemistry. It is quite evident that analytical chemistry has never been served by a more original mind, nor a more prolific pen, than Kolthoff's.

Quite recently Professor Kolthoff was able to implement a long-held urge to provide practicing analytical chemists with a comprehensive, multi-volume reference monograph covering all phases of analytical chemistry. In partnership with Philip J. Elving, and with the collaboration of Ernest B. Sandell, several volumes of this *Treatise on Analytical Chemistry* have already appeared.

It is not uncommon for a gifted research scholar to be indifferent to educational aspects of his field, but here again Professor Kolthoff has been exceptional. Although his chief preoccupation has always been the education (not "training") of graduate students, and during all the years at Minnesota he never taught the elementary analytical course, he has not neglected undergraduate instruction in analytical chemistry. His elementary *Textbook of Quantitative Inorganic Analysis*, co-authored with Ernest B. Sandell, originally published in 1936 and since revised twice, is the comparison standard among American texts on this subject. Kolthoff's classroom teaching has been confined to seminars and to an advanced course devoted chiefly to electrometric methods of analysis. For use in the latter course he published in 1931 a textbook, *The Colorimetric and Potentiometric Determination of pH. Outline of Electrometric Titrations*, and a German translation was prepared the following year with the assistance of Oskar Schmitt. In 1941, in collaboration with Herbert A. Laitinen, a second revised edition appeared under the title *pH and Electro Titrations*.

Kolthoff has been outstanding as a teacher of graduate students; a list of those who earned Master's and Doctor's degrees under his guidance is appended. The analytical chemistry faculties of a surprisingly large number of American universities and colleges (as well as several in other countries) are composed of his former students, by their students in turn, and even by a third generation. His laboratory has also been a Mecca for many foreign post-doctoral fellows, which has further extended his influence in the educational sphere, because most of them returned to academic posts in their own countries.

Professor Kolthoff's deep-rooted concern for freedom of thought and expression, and his abhorrence of dogma in any guise, have always underlaid his relationships with his students. Each student was made to feel that he was a partner, not just a useful pair of hands, and he was given every opportunity to learn to behave as an intellectual equal. Kolthoff kept in close contact with each student's progress by daily, informal conferences. On occasion, these sessions with the "Chief" could be embarrassing, because nothing that the student had (or had not!) done ever escaped his incisive scrutiny. But a knife cannot be sharpened on butter, and the whetting of the younger against the experienced mind was education in its finest sense. Kolthoff never exerted the authority of his experience to "silence" a student, but rather the spirit of these discussions was always "Not *who* is right, but *what* is right". Small wonder that Kolthoff's students became and remain his enduring friends.

The intensity with which Kolthoff concentrates on scientific problems, and on his other intellectual pursuits, demands periodic release in physical activity, and for many years tennis was a favourite means of "letting off steam". Although his highly individualistic style, including ambidextrous use of the racket, may have been more baffling than "polished", it kept his opponent very busy. He enjoys swimming, whether in the bucolic surroundings of a pasture pond on a Minnesota farm, or in the North Sea off a Netherlands beach. Horseback riding has been a lifelong hobby, and his disdain of anything "lukewarm" applies to his choice of mount. On one occasion some years ago the horse won the bout, and the resulting fall produced a crippling spinal injury. However, even before he was able to discard crutches, he was back in the saddle.

Kolthoff's extra-professional contributions to analytical chemistry include service for many years on the editorial boards of Analytical Chemistry and the Journal of the American Chemical Society. He was active in the creation of the Section on Analytical Chemistry of the International Union of Pure and Applied Chemistry, and he has served as President of that section as well as Vice-President of the Union.

In addition to ordinary membership in the American Chemical Society, the Dutch Chemical Society and the Dutch Pharmaceutical Society, Kolthoff is an honorary member of a number of other scientific societies, including the American Pharmaceutical Association, the Society for Analytical Chemistry, Phi Lambda Upsilon, the Spanish Chemical Society, the Finnish Chemical Society, the Peruvian Chemical Society, the Czechoslovak Chemical Society and the Israeli Chemical Society. He is a Fellow of the American Academy of Arts and Sciences, and he has the distinction of being one of the few analytical chemists to achieve election to the United States National Academy of Sciences. He is a foreign member of the Royal Bohemian Academy of Sciences and Fine Arts, of the Royal Flemish Academy of Sciences in Amsterdam, and of the Academy of Sciences in Lisbon.

In 1938 the Netherlands government knighted Dr. Kolthoff an Officer in the Order of Orange-Nassau, and in 1947 he was made a Commander in that Order. He holds the Charles Medal of Charles University in Prague. In 1949 the New York Section of the American Chemical Society conferred on him its Nichols Medal, and in 1950 he was the recipient of the Fisher Award in Analytical Chemistry of the American Chemical Society. In 1954 he became an Honorary Professor of San Marcos University, and in 1955 he was awarded an honorary doctor's degree by the University of Chicago. He received the Anachem Award of the Association of Analytical Chemists (Detroit) in 1961.

Happily, this is only a progress report. May God grant Professor Kolthoff many more years of fruitful labour.

GRADUATE STUDENTS OF IZAAK MAURITS KOLTHOFF

1.	E. J. Amdur	M.S.	1941
2.	Madolyn Youse Babcock	M.S.	1950
3.	Cyrus P. Barnum	Ph.D.	1940
4.	Gordon H. Bendix	M.S.	1938
5.	R. A. Bovey	Ph.D.	1948
6.	R. C. Bowers	Ph.D.	1953
7.	Stanley Bruckenstein	Ph.D.	1954
8.	Albert H. Bushey	Ph.D.	1940
9.	Marion Bushey	Ph.D.	1940
10.	E. M. Carr	M.S.	1952
11.	Chi Chang	Ph.D	1958
12.	M. K. Chantooni, Jr.	Ph.D.	1960
13.	J. F. Coetzee	Ph.D.	1955
14.	Frank T. Eggertsen	Ph.D.	1939
15.	William von Fischer	Ph.D.	1937
16.	C. E. Gracias	Ph.D.	1961
17.	W. F. Graydon	Ph.D.	1949
18.	Frank S. Griffith	Ph.D.	1937
19.	L. S. Guss	Ph.D.	1938
20.	W. E. Harris	Ph.D.	1944
21.	A. C. Holler	B.S.	1947
22.	David N. Hume	Ph.D.	1943
23.	R. A. Johnson	Ph.D.	1949

24. W. F. Johnson	Ph.D.	1949
25. S. E. Khalafalla	Ph.D.	1953
26. C. A. Kelly	Ph.D.	1958
27. L. A. Knecht	Ph.D.	1959
28. Herbert A. Laitinen	Ph.D.	1940
29. W. D. Larson	Ph.D.	1936
30. Thomas S. Lee	Ph.D.	1949
31. D. J. Lehmicke	Ph.D.	1945
32. D. L. Leussing	Ph.D.	1952
33. James J. Lingane	Ph.D.	1938
34. William M. MacNevin	Ph.D.	1936
35. George Matsuyama	Ph.D.	1948
36. D. R. May	Ph.D.	1944
37. Walter J. McCoy	M.S.	1938
38. D. C. McWilliams	Ph.D.	1955
39. A. I. Medalia	Ph.D.	1948
40. Carl S. Miller	Ph.D.	1940
41. I. K. Miller	Ph.D.	1950
42. H. Minato	M.S.	1958
43. D. C. Nelson	M.S.	1957
44. E. R. Nightingale	Ph.D.	1955
45. George Noponen	Ph.D.	1936
46. Stephen S. Ober	M.S.	1952
47. Albert S. O'Brien	Ph.D.	1938
48. Y. Okinaka	M.S.	1957
49. Edward F. Orlemann	Ph.D.	1941
50. D. A. Otterson	M.S.	1947
51. Lyle G. Overholser	Ph.D.	1938
52. E. P. Parry	Ph.D.	1950
53. R. W. Perlich	M.S.	1938
54. Thomas B. Reddy	Ph.D.	1960
55. Warren Reynolds	Ph.D.	1955
56. Bart van't Riet	Ph.D.	1957
57. Ernest B. Sandell	Ph.D.	1932
58. I. Shapiro	Ph.D.	1944
59. Maurice E. Stansby	M.S.	1933
60. Vernon A. Stenger	Ph.D.	1933
61. Nora Tamberg	M.S.	1956
62. C. N. Thompson	M.S.	
63. Paul E. Toren	Ph.D.	1953
64. William J. Tomicek	Ph.D.	1934
65. James I. Watters	Ph.D.	1943
66. D. Weiblen	M.S.	
67. Henry C. Yutzy	Ph.D.	1936

For a complete list of the publications of I. M. Kolthoff see p. 351.

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THE STATUS OF AND TRENDS IN ANALYTICAL CHEMISTRY

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THE DEVELOPMENT OF ANALYTICAL CHEMISTRY AS A SCIENCE

BEFORE a subject becomes a science its development is empirical in nature. Facts must be collected before generalisations in the form of laws and interpretations of the facts can be made. Before chemistry had reached the stage of a science, the empirical work in its early days was mainly analytical in nature. With the spectacular development of physical chemistry in the last quarter of the nineteenth century, analytical chemistry started to lose its historic lustre because analytical chemists continued to practice their subject in an empirical way, without making use of the new laws and theories developed by physical chemists. Academically, analytical chemistry became discredited. It was the famous German chemist Wilhelm Ostwald who, at the end of the last century, established analytical chemistry as a scientific discipline. In the preface of his stimulating book, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, published in 1894, Ostwald made it clear that analytical chemistry was doomed to continue to occupy the subordinate position of a maid-servant for the other branches of chemistry unless the analytical chemists would discontinue teaching their subject solely as an empirical technique and art which requires skill, and would start making use of the experimental developments and theories of physical chemistry. Infrequently physical chemists would describe analytical applications of certain physico-chemical principles, but analytical chemists in those days lacked the background to comprehend their significance. At the end of the last century papers describing the principles of voltammetry, of amperometric, potentiometric and conductometric titrations already were found in the chemical literature, to be "rediscovered" and developed much later, after education in analytical chemistry had become scientific in nature. In fact, most of the early scientific fundamentals of analytical chemistry and the analytical applications of theoretical chemistry have been developed by non-analytical chemists. In addition to the early papers on what is now modern electroanalytical chemistry, the development and understanding of acid-base indicators may be mentioned. At the very beginning of this century analytical chemists empirically knew that weak acids are titrated with a strong base using phenolphthalein as an indicator and weak bases with a strong acid using methyl orange as an indicator. It was only after the introduction of the concept of pH and the detailed description of its colorimetric and potentiometric determination in 1909 by the famous Danish *bio*chemist, S. P. L. Sörensen, that the fundamentals of aqueous acid-base titrations could be understood. Sörensen's paper still belongs to the most fundamental publications on the concept and determination of pH with the hydrogen electrode and with acid-base indicators, and it is as important now as it was in those days. Sörensen also made clear the significance and the meaning of buffer action and he developed a set of buffer solutions, covering the entire pH range in aqueous medium. For many years Sörensen's buffer solutions have served as standards for the colorimetric determination of pH and several other purposes. Again, analytical chemists did not comprehend the significance of Sörensen's pioneer work, and it was not until 1914 when the famous Danish *physical* chemist Niels Bjerrum published his classical monograph, *Die Theorie der alkalimetrischen und azidimetrischen Titrierungen*, that a quantitative interpretation of acid-base equilibria and titration errors in aqueous media became available. In the same year the German *bio*chemist L. Michaelis published his book, *Die Wasserstoffionenkonzentration*, and soon thereafter a monograph on oxidation and reduction potentials. This latter book allowed us to give a quantitative interpretation of oxidation-reduction titrations. It was the well known American *physical* chemist, Joel H. Hildebrand, who published in 1913 his important paper on potentiometric titrations with the hydrogen electrode. It was not an analytical chemist but the American *physiological* chemist, W. Mansfield Clark, who in 1917 added the sulphophthaleins to the series of acid-base indicators.

It is not surprising that the fundamentals of analytical chemistry in those early days were developed by non-analytical chemists. Analytical chemistry was still looked down upon as a maid-servant for the other disciplines of chemistry, and no formal education in analytical chemistry was offered by European universities. All students in chemistry had to learn the practice of gravimetric and titrimetric analysis, which was offered as a laboratory course under the supervision of a teaching assistant. Technical universities in Europe and in several American universities had a chair for analytical chemistry, but the subject was taught in a classical way and its aims were mainly to provide instruction in the technique of the analysis of inorganic constituents and of ores, rocks, industrial products, food stuffs, *etc.*

It was only after about 1920 that analytical chemistry gradually became established as a scientific discipline of chemistry. With some notable exceptions, most universities in the world have chairs now in analytical chemistry, and all students in chemistry now receive education both in classical analytical chemistry and—after a course in physical chemistry—in the principles of physicochemical methods of analysis. Those students who major in analytical chemistry for the Ph.D. are exposed to all aspects of modern analytical chemistry, which includes the determination and study of such properties and quantitative characterisation of such systems which aid, and often are essential in, the solution of analytical problems, and which guide in the development of new analytical methods. "Theory guides and experiment decides."

Complaints are sometimes heard that there is overlapping between teaching and research in analytical and other fields of chemistry. Actually, this is not only an unavoidable but rather a desirable situation. A few examples may illustrate this claim. Chemical equilibria is a subject of importance to inorganic, physical, organic, industrial and biochemists. Its principles are now taught in beginning general chemistry, but the significance of this subject in the various specific fields of chemistry is taught in courses for students specialising in these fields. Before scientific analytical chemistry was recognised in the academic curriculum, principles of chemical equilibria were being taught by physical chemists; such courses did not emphasise their primary importance in, and application to, analytical chemistry. Nowadays the subject has rightfully become part of the curriculum in modern analytical chemistry.

Quite generally, in quantitative chemical analysis we make use of properties which can be measured. All other chemists are interested in properties, but again, courses in modern analytical chemistry must include instruction in the understanding of properties which are important analytically, and laboratory instruction on the measurement of these properties.

All experimental scientists must be acquainted with the fundamentals of instrumentation. In view of the fact that an instrument is needed for the measurement of a property, the subject of instrumentation is of special importance to analytical chemistry. Instruction in instrumentation is now a recognised subject in the analytical curriculum.

All chemists are concerned with various aspects of separations, a subject completely analytical in nature. The Dutch word for chemistry is "Scheikunde," meaning the art and ability of separating. It originated in the sixteenth century when chemistry was mainly analytical in nature. The present chemical literature is replete with papers by organic, inorganic, analytical, industrial, and biochemists dealing with the application of chromatography, ion-exchange, distillation, extraction and other methods of separation in the preparation of pure compounds and the identification and determination of constituents. All chemists, including physical chemists, for their own purposes are concerned with an understanding of the factors which determine the degree of completeness of separations. Would it not be desirable that the theoretical and experimental principles of separation—a subject which is analytical chemistry *par excellence*—be taught to all chemists by analytical chemists? The late Professor Ehrenfest once said that everything which is understood in chemistry is physics. Considering the various disciplines of chemistry it is fair to state that the theoretical fundamentals of analytical, inorganic and organic chemistry are physicochemical in nature. But for obvious reasons we need chemists with a major interest in analytical chemistry to teach analytical chemistry, just as we need inorganic chemists to teach inorganic and organic chemists to teach organic chemistry.

THE STATUS OF MODERN ANALYTICAL CHEMISTRY

It seems fair to state that analytical chemistry started to develop as a science towards the end of the first quarter of this century. Analytical chemists became fully conscious of the fact that for the further growth and expansion of analytical chemistry they had to remain up to date with the discoveries and new theories by other classes of chemists and of physicists, and had to consider their significance for and applicability to analytical chemistry. In the last quarter of a century a host of new nuclear, subatomic, atomic and molecular properties have been discovered, most of which already find analytical applications. Radioactive methods, especially activation analysis in trace analysis, are becoming more and more popular. Nuclear techniques have been introduced for analytical purposes. For example, a new instrument has been made available commercially for the rapid and continuous measurement of moisture in bulk materials, based on the reflection of two different kinds of nuclear radiation. X-ray spectroscopy and fluorescence, microwave spectrophotometry, ion-scattering methods, mass spectroscopy and nuclear and electronic magnetic resonance are some of the modern developments which find analytical use. Most of these new techniques originate with physical chemists or physicists, but analytical chemists play an important part in their further development. Numerous symposia organised jointly by physical and analytical chemists are indicative of the role which analytical chemists play in the development of these new techniques.

These advances in techniques are being made possible, not only by new discoveries and theories, but also by the phenomenal progress of instrumentation. This progress has its impact both on the development of techniques based on new discoveries, and also on the development of techniques based on the measurement of a host of classical properties. Many of these properties were known and measured more than a century ago. However, their application to analytical chemistry remained limited, mainly for the reasons that a thorough knowledge and understanding of the instruments was necessary, and the measurements themselves were very time-consuming. Modern instrumentation has changed all this and has even provided us with a host of automatically indicating instruments.

A few examples may illustrate how modern instrumentation has made possible daily measurement of classical properties and their much expanded use in analytical chemistry. Some twenty-five years ago many of us strained our eyes with a Duboscq or another visual colorimeter, or with a polarimeter or refractometer. Accurate spectrophotometers were available as far as colorimetry was concerned, but they were not suitable for routine work. Nowadays modern spectrophotometers for measurements in ultraviolet, visible and infrared light, and also self-recording instruments, are found in all modernly equipped analytical laboratories. Similarly, the analytical application of emission spectroscopy probably dates back to Fraunhofer, who in 1817 combined a slit, a glass prism and a theodolite. This same scientist may be considered the father of atomic absorption (Fraunhofer lines). Bunsen is usually credited as the chemist who introduced spectroscopy in analytical chemistry when he wrote with Kirchhof his classical paper in 1860 entitled *Chemische Analyse durch Spektralbeobachtung*. Much later the spectrograph was developed, but did not acquire popularity until 1939 when excellent optical instruments were produced which allow comparison of spectra with a microphotometer that can be coupled to a recorder—the latter in turn automatically recording the intensity of a whole series of lines.

Quite generally, recorders are now being used in analytical chemistry for automatic registration. Classical photometric, potentiometric, coulometric, conductometric, amperometric, turbidimetric and thermometric titrations are now being carried out with automatic end-point determination. Principles of coulometry, including stripping analysis, and coulometric titrations were laid down more than a hundred years ago in Faraday's second law, but their practice has become popular only after the development of convenient instruments.

Most modern methods of separation are classical in nature. The first evidence of the use of paper chromatography as a separation technique is found in the dye industry of the 1800's. Dyes were tested by spotting vat solutions on paper and observing the number of concentric rings formed as the liquid migrated. The German dye chemist, F. Runge, developed this technique and described the results in two books, *Farbenchemie* (1850) and *Der Bildungstrieb der Stoffe*, the latter being prefaced by actual chromatograms developed by Runge.

Schönbein, around 1860, showed that if a paper is dipped into an inorganic salt solution the liquid migrating through the paper carries the salt with it. However, the water moves faster than the inorganic salts, which travel with different rates. F. Goppelsröder developed the method further for the detection and determination of inorganic and organic constituents, and called the technique capillary analysis. This technique is closer to adsorption than to partition chromatography. Columnar chromatography was discovered in 1897 by the American, J. T. Day, who used it for fractionating petroleum by preferential adsorption on columns of Fuller's earth. Ion-exchange chromatography is classical in nature, and has been made use of in soil studies since the middle of the last century. Liquid-liquid extraction was used already in the 19th century as a method of separation. All these methods of separation have been greatly perfected in the last 25 years, and new techniques, like partition chromatography (Martin and Synge, 1941) and gas chromatography (James and Martin, 1952) have been added. In spite of the great popularity of all these methods of separation, and the great number of papers on the subject in contemporary chemical literature, many phases of these techniques are still incompletely understood.

It is hardly necessary to mention that modern analytical chemistry is still actively engaged in the further development of classical analytical principles. Organic reagents for the detection and determination of inorganic constituents had already been introduced in the 19th century. Many analytical chemists have been searching since for organic reagents with such functional groups that they become selective and/or specific for any given cation. That goal probably never will be reached because, considering the structure of the ions, it would seem impossible that there is a reagent which is truly specific for one particular ion and the reaction of which is not interfered with by some other element. However, the ideal goal may be approached with the aid of masking reagents and modern methods of separation. There is already a considerable literature on the use of ethylenediaminetetra-acetate (EDTA) and similar compounds for masking purposes. Frequently, reports on the discovery of known reagents, or the introduction of known compounds as reagents for use in various types of methods of chemical analysis, are found in the modern literature. Some of these reagents may have been known for years but had not been tested for their analytical usefulness. With our increasing knowledge and understanding of chemical bonding, of steric hindrance and of co-ordination in particular, it is now often possible to predict which groups may have desirable properties for particular analytical purposes, for example, for complexation. Although EDTA and related compounds had been known for some time, it is only as a result of the pioneer work of Gerold Schwarzenbach that they are now in daily use in complexometric titrations and for masking purposes. A large chapter has been added to analytical chemistry after the introduction of these reagents.

RESEARCH IN ANALYTICAL CHEMISTRY

Academic and industrial analytical research deals with the theoretical and experimental development of classical and modern techniques, including micro and submicro techniques, the interpretation and improvement of existing methods of analysis, the development of new methods of analysis to replace existing ones, and the assay and evaluation of new industrial products.

As far as research dealing with theoretical fundamentals is concerned, there naturally is again overlapping with some phases of research carried out by physical, inorganic and organic chemists. As a matter of fact, in the last quarter of a century there has been a definite shift of the activities of classical physical chemistry to analytical chemistry. In the beginning of this century the determination of the dissociation constants of acids and bases by potentiometric, conductometric and colorimetric methods, the determination of distribution equilibria, of solubility products, of the stability constants of complexes, of oxidation-reduction equilibria, of electrode potentials, *etc.*, belonged to the activities of the physical chemists. Nowadays this type of information is obtained mainly by analytical and inorganic chemists. A great many phases of electrochemistry have become the domain of the analytical chemist. In order to interpret and further develop empirical methods of analysis it is essential that the physical chemistry involved in the behaviour of the components of the systems under consideration be fully understood. For example, acid-base titrations in non-aqueous media have experienced wide analytical application after the publication of the fundamental papers by Conant *et al.* on the behaviour of bases in pure acetic acid. Titrations of acids and of bases in a host of other solvents have been described since. However, although the results can be understood qualitatively, much work on acid-base equilibria remains to be done to arrive at a quantitative understanding. The same is true for many phases of extraction analysis as far as a quantitative interpretation of distribution equilibria is concerned. Electroanalytical methods in non-aqueous media, including fused salts, require much fundamental research before they can be fully developed. A host of problems in all kinds of solvents demands much fundamental research before they are completely understood and the results can be applied to further improvement of analytical methods.

Consider, for example, our understanding of the formation and growth of precipitates, of coprecipitation and aging. In spite of the numerous publications dealing with these subjects, a quantitative understanding of the factors determining or affecting the size of the particles of a precipitate and of coprecipitation is still lacking. This is also true with regard to an understanding of the value of the distribution coefficient (or constant), λ, in the formation of heterogeneous mixed crystals. Theoretically, λ should be equal to the thermodynamically defined homogeneous distribution coefficient, D. But even under conditions of *kinetically controlled precipitation*, a term which I prefer to "precipitation from homogeneous solution," λ can be much greater or much smaller than D, even though in many systems studied, especially by L. Gordon, λ is found to be sensibly constant during the precipitation. Apparently, supersaturation during the growth of crystalline particles is mainly responsible for the difference between D and λ (J. A. Hermann, 1956). In unpublished work we have found that λ closely approaches D in the kinetically controlled formation of mixed crystals of barium and lead sulphate, with barium sulphate as the host crystal, when the system is seeded with a relatively large amount of small and well aged crystals of barium sulphate. These crystals serve to overcome to a large extent the supersaturation during the formation of mixed crystals.

In the development of new chelating agents, including metal ion indicators, the modern investigator is actively interested in the nature of reactive groups and the structure of chelates. In order to predict and interpret complexometric titration curves he must have data on stability constants and quantitative knowledge of the effect of pH and other constituents on equilibria. In addition, knowledge of the kinetics of formation of the dissociation of metal chelates, of the chromatographic (ion exchange) and other characteristics of metal chelates, are essential in the further development of the application of complexation in analytical chemistry. Research on ion exchange, chromatography, solvent extraction, electrodialysis and migration, again, is being carried out not only by analytical chemists but also by physical, inorganic, organic, industrial and biochemists. This overlapping of research activities is a fortunate situation, because all disciplines of chemistry profit from each other's contributions, and together we can fill up the gaps in our understanding of the fundamentals of chemistry. It would be deplorable if the scope of research in analytical chemistry were limited to the more typically classical topics.

ACADEMIC AND INDUSTRIAL ANALYTICAL CHEMISTRY

From what has been said in previous sections we may define academic analytical chemistry as the science concerned with the study and interpretation of all aspects of existing methods of analysis and the development of new methods of analysis. This definition apparently has neither the sympathy nor the approval of industrial analytical chemists. In his thought-provoking Fisher Award Address, H. A. Liebhafsky[1] refers to a definition of analytical chemistry which I stated twelve years ago:[2] "The aims and objectives of analytical chemistry are to determine the composition of any complex compound or mixture of compounds." Generously Liebhafsky adds: "From a university point of view of twelve years ago, this is an excellent definition," I would like to maintain that academically the definition is as valid now as it was a century ago. Liebhafsky then refers to R. C. Chirnside's interesting address[3] entitled *The Enlargement of Horizons in Analytical Chemistry*, in which Chirnside quotes E. B. Hughes as having defined our discipline to be "the examination of a material to ascertain its composition, its properties, its qualities." Liebhafsky finds this definition too restrictive and sees "modern analytical chemistry as the characterisation and control of materials—no more, and certainly no less." Liebhafsky further makes the statement (p. 26A): "Analytical chemistry has lost prestige as a research activity and has not yet gained prestige commensurate with its great and growing importance as a *service in industry*." (Italics mine). I would infer from this statement that Liebhafsky expresses himself on the *role* of analytical chemistry and the *use* of analytical chemistry in *industry*. His views are in close sympathy with those of Chirnside, another recognised analytical-chemical leader in industry, who states: "... he would be a brave man who would today attempt a proper definition of analytical chemistry or chemical analysis, or indeed a description of the analyst himself."

If it is admitted that the classical definition of analytical chemistry has remained unchanged but that the aims and objectives for which the analytical chemist is used in industry have changed and are continuing to change, the question arises whether our education of majors with an advanced degree in analytical chemistry satisfies the needs of industry. If the present education of our majors for the Ph.D. in analytical chemistry does not provide adequate background for the industrial analytical chemists, our institutions of higher learning might consider the introduction of a new minor in "materials characterisation and control" for our majors in analytical chemistry. As far as the loss of prestige as a research activity is concerned, I would like to claim that particularly during the last twenty-five years analytical chemistry has gained great prestige as a research activity, thanks to fundamental contributions by both academic and industrial analytical chemists. To a large extent the empiricism has gone out of analytical chemistry.

RECENT AND FUTURE TRENDS IN ANALYTICAL CHEMISTRY

Education in chemistry

In this era of spectacular advances in the natural sciences, and in chemistry in particular, each discipline of chemistry must periodically reappraise and modify its curriculum in order to keep it up to date with the developments. During the last few years we have witnessed and are still witnessing such a reappraisal and modernisation of courses, especially in the U.S.A. In order not to extend the number of years required now for earning a bachelor's or an advanced degree, all disciplines must curtail their "classical" programmes so that justice can be done to the teaching of modern developments. Reluctantly, analytical chemists internationally agree that the scope of the classical programme in gravimetric and titrimetrc analysis, and in particular the laboratory work, must be curtailed, in order to include the theoretical and experimental fundamentals of physicochemical methods of analysis in the curriculum of all students in chemistry. With further scientific developments periodic modernisation of courses will remain necessary.

However, training in elementary gravimetric and titrimetric analysis should remain a requirement in the curriculum for all chemists, as these subjects have not outlived their usefulness. In experimental research in all fields of chemistry these methods find frequent application, *e.g.*, in testing for purity of and assaying reagents, and in following the course and rate of reactions. Moreover, gravimetric and titrimetric analysis are still indispensable in the accurate determination of major constituents in many types of samples. Also, in several physicochemical methods standards are necessary whose composition is often determined by classical analysis, while some "instrumental methods" also involve classical methods, like gravimetry in activation analysis.

As far as majors for the Ph.D. in analytical chemistry are concerned, it is still desirable to include the essentials of classical analytical chemistry and it is possible to cover the essentials of modern analytical chemistry in the curriculum. Considering however, the almost frightening expansion of the literature, the appearance of a host of new journals in specialised fields of analytical chemistry, it will become necessary to add more specialists to the teaching staff. Even so, the education should remain fundamental in nature, and should provide such background that the Ph.D. can later become a specialist in particular fields. Many of us know by experience that education does not stop at the Ph.D. level. A recent Ph.D. is a novice in the field who has such knowledge and understanding of all aspects of analytical chemistry that it serves him to develop into a creative academic or industrial analytical chemist. Only those of our graduate students who exhibit great ability and creativity in research—and their percentage is rather small—should be encouraged to work for the doctor's degree. Society has a great need for advanced technicians who might be encouraged to earn a new degree of "Chem.D." (chemical doctor).

Future trends in analytical chemistry

The Dutch have a saying: "In the past lies the present, and in the present what is going to be." Considering the past and present development of analytical chemistry it is possible to forecast future trends without becoming speculative. In this era of concentration on the natural sciences, discoveries of new properties, especially in the field of radiation, will continue to be made. Modern instrumentation will quickly provide the instruments with which these properties can be measured and recorded. Thus, we will experience a further expansion of "physical analysis." This, combined with continued automation of new and classical methods of analysis may create social problems. However, for the development of scientific analytical chemistry the further perfection of instrumentation is most welcome, because the results of measurements will become more readily available and more time and effort can be devoted to the solution of unsolved problems.

More and more use will be made of computers in the solution of several analytical problems. In titrations involving complicated equilibria exact equations can be derived for the calculation of the titration error and titration curves, for example, in many complexation reactions or acid-base equilibria and titrations in solvents of low dielectric constant. Such equations may be so involved that they require computers for their exact solution. The same is true in the analysis of complex organic mixtures by measuring a host of physical properties, or in the further development of "kinetic" analysis based on different rates of reaction of various constituents, or the determination of particle size and particle size distribution by light scattering and other methods.

In the previous sections a few examples of the application of chemical reactivity have been given. Several methods based on reactivity are awaiting further development; others have hardly been explored yet. The search for more selective reagents, including complex-formers, particularly those with mixed ligands, and for metal ion indicators is not nearly finished. In organic analysis, research continues on specific reagents for functional groups, and on making more analytical use of the kinetics of formation of compounds obtained by reaction of functional groups with suitable reagents, and of the kinetics of the dissociation of these reaction products into the original reactants. Further studies on the expansion of oxidation-reduction analysis to solutions in solvents much more difficult to oxidise and/or reduce than water, remain to be done.

Our quantitative knowledge of the fundamentals of the titration of Lewis acids with bases is still extremely incomplete. The formation constant of the "neutralisation product" AB formed by reaction of the Lewis acid A with a base B, its ionic dissociation constant, its molecular dissociation constant, and the association constants of the ionic dissociation products of AB with AB in a variety of solvents, should be known before a successful interpretation and exhaustive development of thermometric, conductometric, potentiometric (search for indicator electrodes), amperometric, coulometric and visual titrations of Lewis acids (including many inorganic ions or compounds) with bases can be made.

For further development of extraction analysis, much more research remains to be done on formation constants of ion pairs, of ion triplets and quadruplets in solvents used for extraction, and on the effects of pH and of structural characteristics of the cations and anions on distribution and extraction coefficients.

Little work has been done on reactivity at very high and at very low temperatures, on the use of various radiations to bring about chemical reactions, on the quantitative measurement for analytical purposes of the energy involved in breaking chemical bonds.

Organic, inorganic and industrial chemists continue to make available a host of new organic and inorganic compounds. In consequence, analytical chemists are being called upon continuously to devise methods of analysis for these compounds. In addition, analytical chemists are interested in the possible use as reagents of the new products, like organo-metallic compounds. Continuously industry is producing new complex products, like inorganic and organic polymers, and semiconductors, which demand the development of analytical methods for their characterisation and evaluation, and the solution of analytical problems during the production process. Semiconductors are an example *par excellence* to illustrate the increasing demand for the development of new methods for trace analysis, and for the preparation of substances of extremely high degree of purity. Modern biochemistry requires the further development of sub-micro techniques of analysis.

The above review of present and future activities in analytical chemistry is sketchy in nature. In an essay of this kind it is not possible to present either an exhaustive or complete discussion of these activities. However, the examples given substantiate the thesis that analytical chemistry will continue to flourish as one of the scientific disciplines of chemistry as long as there are unsolved chemical problems and the chemistry remains in chemistry.

LITERATURE CITED

[1] H. A. Liebhafsky, *Analyt. Chem.*, 1962, **34**, 23A.
[2] I. M. Kolthoff, *Chem. Eng. News*, 1950, **28**, 2882.
[3] R. C. Chirnside, *Analyst*, 1961, **86**, 314.

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DETERMINATION OF URANIUM AT MICROGRAM LEVELS BY DERIVATIVE POLAROGRAPHY*

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Summary—The incremental method of derivative polarography has been applied to the low-level analysis of uranium in acetate-buffered EDTA electrolyte. Optimum conditions are shown for the rapid determination of $2 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ bismuth and of $5 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ molybdenum, with a precision $\leq 2\%$ and without prior separation. Uranium in amounts $\leq 10\ \mu g$ may be detected in a 10^4-fold excess of bismuth. The method has been used successfully for the analysis of a bismuth alloy containing 0·1% of uranium.

URANYL ion is one of the few electroactive species which are only weakly complexed by ethylenediaminetetra-acetate (EDTA) and related chelating agents. This fact has prompted Přibil and Blažek,[1] in the course of systematic studies, to investigate the polarography of uranium in an EDTA-containing medium; procedures were reported for determining uranium in the presence of several elements whose half-wave potentials are markedly displaced towards negative values by virtue of chelation with EDTA. Davis[2] has made a more fundamental study of the uranyl-EDTA system. Conventional techniques were used in these earlier investigations and the various elements were present at comparable levels. Derivative polarography, on the other hand, with its enhanced sensitivity and resolving power, has proved ideally suited for the determination of minor constituents in the presence of a less easily reduced major constituent. It was felt, therefore, that derivative polarography in solutions containing EDTA could be made the basis of a simple and rapid analytical method for micro amounts of uranium in a variety of matrices, without prior separation. It is shown in the present paper that the incremental polarograph[3] may be used to determine less than $5 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ bismuth or molybdenum, with a precision $\leq \pm 2\%$. This application is typical of the analytical problems created by developments in nuclear technology.

EXPERIMENTAL

Apparatus

The incremental polarograph has been described in detail,[3] and shown to provide an excellent novel approach to derivative polarography. The present work was carried out using a modified version, which includes transistorised operational amplifiers (Philbrick P2) of exceptionally low inherent noise level and a timing section of greatly improved precision and versatility. The current amplifier provides sensitivities ranging from 0·25 to 50 μA full-scale, and the current differences stored in the memory capacitor can be amplified by factors ranging from 10 to 500. The modified instrument also incorporates optional circuitry for controlled-potential polarography,[4] involving the use of a three-electrode system.

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* This work was performed under the auspices of the U.S. Atomic Energy Commission.

In the present work, unless otherwise specified, the current was sampled during the period from 3·0 to 3·6 sec after drop fall (drop time *ca.* 5–5·5 sec, m = 1·46 mg/sec). The voltage was scanned in 10-mV increments. Polarograms were recorded by means of a Leeds and Northrup Speedomax recorder (Model G, 0·25-sec pen speed), using the duplex readout mode, which allows simultaneous recording of the current amplifier output over the sampling period and of the difference amplifier output corresponding to the end of the sampling period. This feature is of interest because it allows measurements, on the same polarogram, of both the peak incremental response (*i.e.*, the slope of the current-voltage curve at the half-wave potential) and the instantaneous diffusion current, at the same instant in the drop life; the relationship between these quantities is useful either as a criterion of reversibility or as a means for determining *n* in reversible systems.

Reagents

Stock solutions of uranyl perchlorate were prepared from U.S. Bureau of Standards U_3O_8 and standardised coulometrically. Bismuth stock solutions were obtained by dissolving analytical reagent bismuth trioxide in excess nitric acid, and $(NH_4)_6Mo_7O_{24} . 4H_2O$ served as a source of molybdenum. Solutions of EDTA were standardised titrimetrically against standard magnesium chloride. Triple distilled mercury was passed through a nitric acid purification column before use.

Because of the necessity for minimising the level of copper impurities (*vide infra*), the available distilled water was purified further using a commercial distilling-refluxing unit.

General procedure

The polarographic cell consisted of a jacketed beaker, placed on a triple shock mount and maintained at 25° by water from a circulating constant temperature bath. This was preferable to direct immersion in a water bath because it was found essential to minimise sources of electrical noise. The cell was covered with a polyethylene stopper containing appropriate openings. Contact to the saturated calomel reference electrode was made through a fine porosity frit. The three-electrode configuration, with a platinum spiral counter electrode, was used in most of the work, although *iR* corrections were, as expected, wholly negligible at concentrations less than $2 \times 10^{-4}M$. Oxygen was removed from the solutions with prepurified nitrogen which was bubbled through dilute vanadium^{II} perchlorate.

Incipient maxima interfered with measurements of the peak incremental response even in $2 \times 10^{-5}M$ uranium solutions; thymol was therefore used at a concentration of 0·001%, which suppressed the maxima without producing distortion in the diffusion current region. Use of Triton X-100 cannot be recommended, despite its masking effect on the interfering copper wave[5] (*vide infra*), because it was found to attenuate the uranium wave markedly as well.

In order to minimise introduction of impurities, no effort was made to maintain the ionic strength constant by adding excess inert salt. The work was performed at ionic strengths varying from 0·1 to about 0·3, and it was ascertained that this variation had no noticeable effect on the behaviour of uranium. All EDTA concentrations quoted refer to the excess over the stoichiometric amount required by the metal ion(s) present. Potentials are referred to the saturated calomel electrode.

RESULTS AND DISCUSSION

Uranium alone

Some of the interesting aspects of the polarography of uranyl-EDTA complexes have been discussed by Davis,[2] who worked in a self-buffered 0·1*M* EDTA-1*M* sodium perchlorate supporting electrolyte. He obtained a single wave, the shape of which points to a reversible *one-electron* reduction. His results in a weakly acidic medium, however, led to diffusion current constant values substantially larger than would be expected on this basis, and he also found that massive reduction at a mercury pool proceeds by a *two-electron* step, *i.e.*, to uranium^{IV}. We have observed similar behaviour in a supporting electrolyte consisting of either 0·001*M* or 0·01*M* excess EDTA and 0·1*M* acetic acid—0·1*M* sodium acetate buffer (referred to hereafter as "0·1*M* acetate buffer"). In fact, the presence of acetate buffer was found to enhance the diffusion current constant still further. This is shown in Table I; the diffusion current constants, *I*, were calculated from instantaneous diffusion currents, i_d, corresponding to time t (the end of the sampling period), and converted to average values:

$$I = \frac{\frac{6}{7} i_d}{Cm^{2/3}t^{1/6}}.$$

From an analytical viewpoint, a medium containing 0·1*M* acetate buffer provides an appreciable gain over the sensitivity attainable with EDTA alone, and it was used throughout most of this work. The half-wave potentials of uranium under these conditions are —0·30 V and —0·31 V in 0·01*M* and 0·001*M* excess EDTA, respectively. Indications are that the slight negative shift is caused by competing acetate complexation at the lower EDTA concentration. Further work is in progress on the significance of these findings.

The relationship between peak incremental response and concentration was found to be linear over a range of uranium concentrations from $5 \times 10^{-6}M$ to $8 \times 10^{-4}M$, the slope being (0·47 ± 0·01) μA/m*M* per 10-mV step. Within this range, concentrations were determined with a precision of ±1%. Below $5 \times 10^{-6}M$ the presence of copper impurities in the water interfered to a degree with the quantitative determination of uranium, although concentrations as low as $1 \times 10^{-6}M$ could be detected. Copper forms an EDTA complex which is reversibly reduced to the metal;[6] thus, copper peaks were observed in the supporting electrolyte at —0·24 V and —0·27 V, respectively, with 0·001*M* and 0·01*M* EDTA. Regular distilled water proved entirely inadequate for work below $2 \times 10^{-5}M$ uranium. Even by using redistilled water it was impossible to reduce the height of the residual copper peak beyond a value about 40% in excess of the base line level (0·0015–0·002 μA per 10-mV step[3]). This corresponds to an estimated decrease in copper concentration from $5 \times 10^{-6}M$ to $8 \times 10^{-7}M$. The limitation introduced by residual copper is illustrated in Fig. 1. In 0·001*M* EDTA, where the half-wave potentials differ by 0·07 V, an indication of a copper shoulder can be seen on the ascending edge of the uranium peak, producing slight asymmetry. In 0·01*M* EDTA, however, the half-wave potentials are separated by only 0·03 V; here the waves essentially overlap, and copper definitely contributes to the uranium peak height. It should be noted that the 0·03 V separation in half-wave potentials produces a shift of the observed peak from —0·30 V towards —0·27 V as the uranium concentration approaches the residual copper level; errors will result under such conditions if the incremental response is measured at the composite peak location rather than at the true half-wave potential as established at higher concentrations.

TABLE I.—POLAROGRAPHY OF URANIUM IN EDTA-CONTAINING MEDIUM (pH = 4·55 ± 0·05; 0·001% OF THYMOL PRESENT)

$U \times 10^3$, *M*	EDTA, *M*	*I*	Remarks
0·82	0·01	2·52	0·1*M* acetate buffer present
0·82	0·01	2·27	0·1*M* $NaClO_4$ present[a]
0·41	0·1	2·18	No additional supporting electrolyte present[a]

[a] pH adjusted using HCl and NaOH.

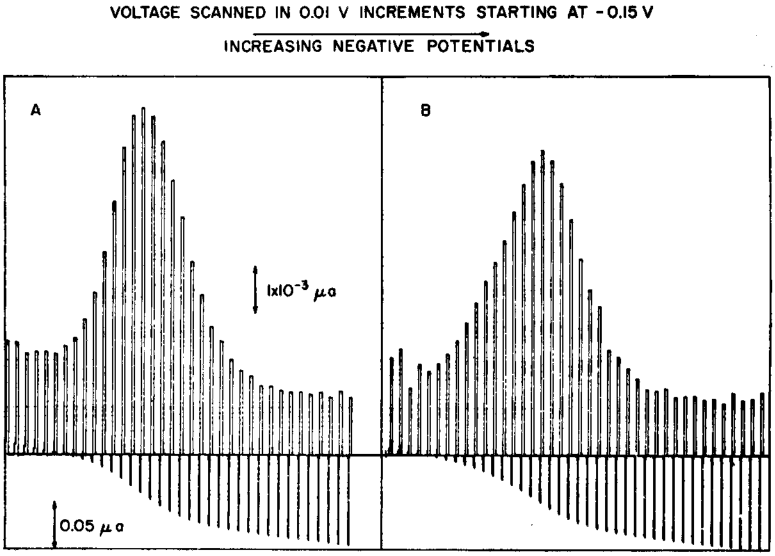

FIG. 1.—Effect of EDTA Concentration on Polarography of Uranium (1 × $10^{-5}M$ U; 0·1M CH_3COOH–0·1M CH_3COONa; 0·001% thymol):
(A) 0·01M EDTA, (B) 0·001M EDTA.
Current-voltage curve is recorded below base line, simultaneously with incremental curve.

Uranium-bismuth and uranium-molybdenum-mixtures

Fig. 2 shows a polarogram of a solution containing 1 × $10^{-4}M$ each of uranium and of bismuth in the EDTA electrolyte. The bismuth wave is seen to be composed of two separate waves under these conditions; the same behaviour was observed with 1 × $10^{-3}M$ bismuth. It may be noted that, although the bismuth-EDTA complex is known to be reduced irreversibly,[7] the existence of two nearly overlapping waves of this type can only be established by a derivative technique. Neither location nor height of the uranium peak, however, were affected by the presence of bismuth, and the separation between the uranium half-wave potential and the first bismuth peak is more than 0·2 V. The irreversible nature of the bismuth wave makes quantitative calculations difficult, but it is apparent that large bismuth/uranium ratios can be tolerated without causing appreciable interference with the uranium peak. Fig. 3 illustrates the polarographic behaviour of a solution containing 1 × $10^{-5}M$ uranium in the presence of 0·01M bismuth and 0·01M excess EDTA. Excellent resolution is achieved between the uranium peak and the ascending edge of the bismuth wave. The resolution is slightly less satisfactory with 0·001M EDTA, where the uranium half-wave potential is 0·01 V more negative. No further improvement was noted at EDTA concentrations higher than 0·01M in either the presence or absence of acetate buffer.

Curve (A) in Fig. 3 shows the extent of interference of the aforementioned residual copper wave. In the presence of 0·01M bismuth the copper wave was found to behave irreversibly; the copper peak was displaced to —0·29 V, *i.e.*, to within 0·01 V of the uranium peak, and its location became independent of the excess EDTA concentration. This observation was not investigated further at this time; however, the effect facilitates low-level uranium analysis, as does the relatively flat region beyond the

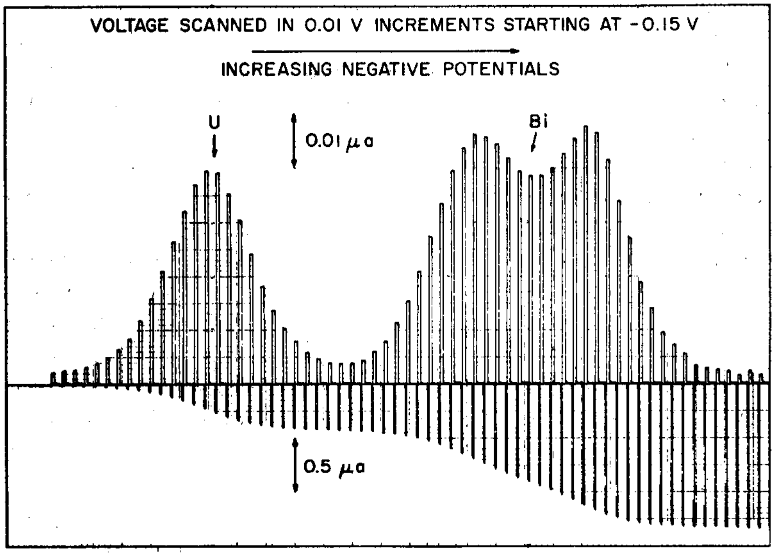

FIG. 2.—Polarogram of a Uranium-Bismuth Mixture (0·82 × $10^{-4}M$ U, 1 × $10^{-4}M$ Bi; 0·01*M* EDTA, 0·1*M* CH_3COOH–0·1*M* CH_3COO Na, 0·001% thymol).

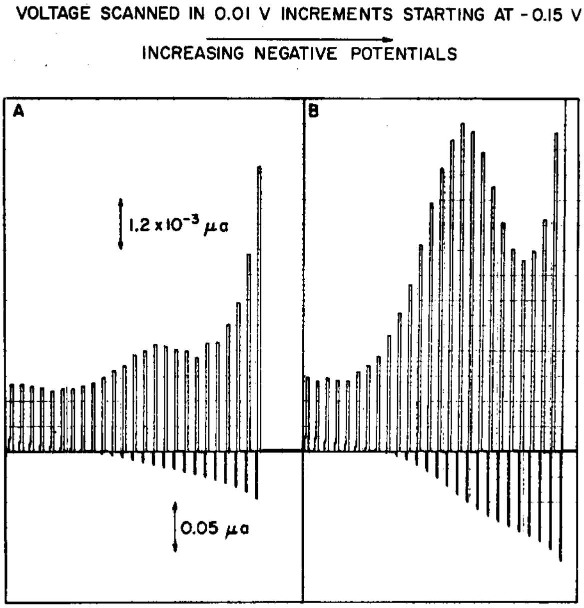

FIG. 3.—Polarogram of Uranium in Presence of Excess Bismuth:
(A) Supporting electrolyte: 0·01*M* Bi, 0·01*M* EDTA,
0·1*M* CH_3COOH–0·1 *M* CH_3COONa, 0·001% thymol.
(B) Same, plus 1 × $10^{-5}M$ U.

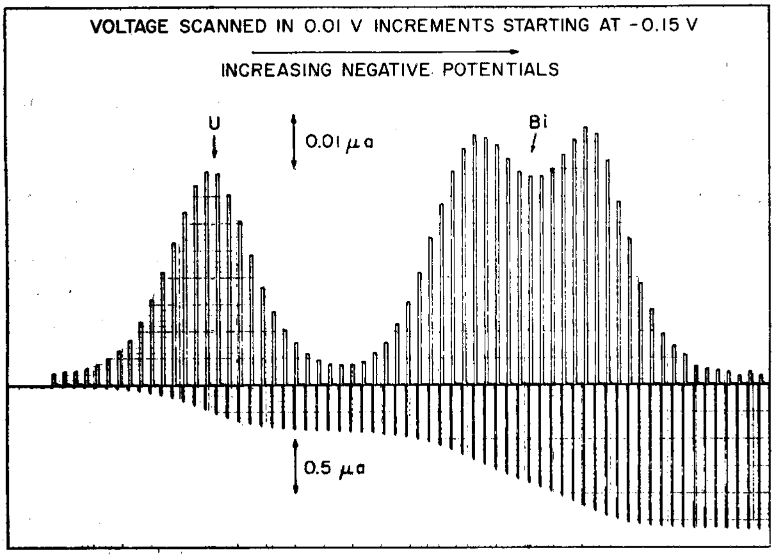

FIG. 2.—Polarogram of a Uranium-Bismuth Mixture (0·82 × $10^{-4}M$ U, 1 × $10^{-4}M$ Bi; 0·01*M* EDTA, 0·1*M* CH_3COOH–0·1*M* CH_3COO Na, 0·001% thymol).

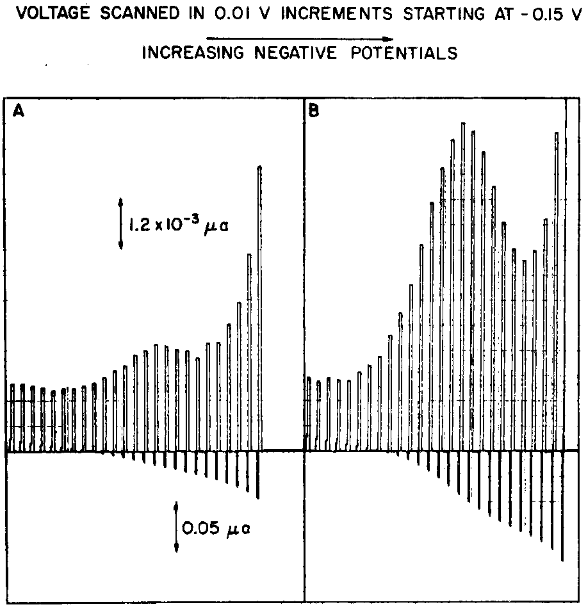

FIG. 3.—Polarogram of Uranium in Presence of Excess Bismuth:
(A) Supporting electrolyte: 0·01*M* Bi, 0·01*M* EDTA, 0·1*M* CH_3COOH–0·1 *M* CH_3COONa, 0·001% thymol.
(B) Same, plus 1 × $10^{-5}M$ U.

copper peak, caused by the onset of the bismuth wave. Thus, $2 \times 10^{-6}M$ uranium in $0{\cdot}01M$ bismuth could be determined with a precision of ±1%, and $1 \times 10^{-6}M$ uranium (corresponding to a 25% increase over the residual copper peak) could easily be detected. Linearity of the peak incremental response, to within ±2%, was established over the $2 \times 10^{-6}M - 1 \times 10^{-4}M$ concentration range; the slope was found to be *ca.* 7% lower than in the absence of bismuth.

Molybdenum in the same supporting electrolyte was found to give two fairly well-resolved peaks, between −0·55 V and −0·75 V. This observation basically confirms the findings of Pecsok and Sawyer,[8] and again serves to demonstrate the utility of the incremental approach in analysing complex waves. The presence of $10^{-5}M$ molybdenum did not affect either location or height of the uranium peak. Molybdenum at a concentration of $10^{-2}M$, however, caused difficulties because of the onset of a drawn out wave at −0·26 V, *i.e.*, 0·04 V more positive than the uranium peak. The situation could be improved by increasing the excess EDTA concentration to $0{\cdot}05M$ ($0{\cdot}1M$ acetate buffer), thereby shifting the onset of the molybdenum wave to −0·33 V. Under these conditions $5 \times 10^{-6}M$ uranium could be determined in the presence of $10^{-2}M$ molybdenum with ±2% precision, using the peak observed at −0·31 to −0·32 V; this corresponded to a 50% increase over the residual response. Linearity was established up to $1 \times 10^{-4}M$ uranium, with a slope of 0·42 μA/mM, *i.e.*, 10% lower than for uranium alone.

Practical application

To test the practical utility of the technique described, uranium was determined in an alloy containing more than 99·8% bismuth. This material has been studied extensively as a potential liquid homogeneous reactor fuel. It also contains 0·035% of zirconium, 0·025% of magnesium and smaller traces of steel corrosion products. The following procedure was employed:

Dissolve a 6 to 8-g sample in excess nitric acid. Transfer the solution to a 200-ml volumetric flask and make up to volume. The final solution should contain *ca.* $1M$ nitric acid to prevent hydrolysis of bismuth on standing. Transfer a 5·0-ml aliquot to a 100-ml volumetric flask containing 10 ml of $1M$ acetate buffer. Add enough $1M$ sodium hydroxide to neutralise excess nitric acid. Add 10 ml of $0{\cdot}10M$ EDTA *in excess* over the amount required (*ca.* 10 ml) to dissolve the precipitate formed in the neutralisation step. Add 0·5 ml of 0·2% alcoholic thymol solution and dilute to the mark. The final pH should be 4·6 ± 0·1. Transfer a portion to the polarographic cell, de-aerate and obtain the incremental polarogram. Measure the incremental response at −0·30 V *vs.* S.C.E. Calculate the uranium concentration with the aid of a blank and appropriate uranium standards, both containing the same concentrations of bismuth, EDTA and buffer as the sample. Double or triple distilled water should be used for both preparation of reagents and all other operations.

Four separate portions of an alloy of this type (kindly provided by Dr. J. R. Weeks) were analysed by the above procedure, yielding 0·096% of uranium with an average deviation of ±2%. A modified version of the spectrophotometric dibenzoylmethane method[9] gave 0·102%, with comparable precision. It should be noted that the spectrophotometric procedure includes a preliminary extraction step. By contrast, the present method involves only the most elementary chemical steps; it is therefore easily applicable to a highly radioactive material, as would be exemplified by the above prospective reactor fuel.

In conclusion, it is shown that the incremental technique of derivative polarography can be applied to rapid and precise low-level uranium analysis in systems of high electrochemical complexity, without the need for prior separations.

Zusammenfassung—Die Methode der Inkremente in der Derivativpolarographie wurde auf die Bestimmung geringer Uranmengen in acetatgepuffertem EDTA-Elektrolyten angewandt. Die optimalen Bedingungen für die Schnellbestimmung von $2\cdot10^{-6}$m Uran neben 0,01m Wismut und $5\cdot10^{-6}$m Uran neben 0,01m Molybdän werden angegeben. Die Genauigkeit ist besser als 2%, vorherige Abtrennung nicht notwendig. Uranmengen unter 10 μg lassen sich neben der 10^4-fachen Menge Bi nachweisen. Die Methode wurde mit Erfolg auf die Analyse einer 0,1% U enthaltenden Wismutlegierung angewandt.

Résumé—La méthode à incréments de la polarographie dérivée a été appliquée à l'analyse de traces d'uranium dans un électrolyte constitué par de l'EDTA tamponné par de l'acétate. Les conditions optimales sont indiquées pour la détermination rapide d'uranium $2 . 10^{-6}$ M en présence de bismuth 0,01 M et d'uranium $5 . 10^{-6}$ M en présence de molybdène 0,01 M avec une précision $\leqslant 2\%$ et sans séparation préalable. L'uranium en quantité inférieure ou égale à 10 μg peut être détecté dans un excès de 10^4 de bismuth. La méthode a été utilisée avec de bons résultats dans le cas de l'analyse d'un alliage de bismuth contenant 0,1% d'uranium.

REFERENCES

[1] R. Přibil and A. Blažek, *Coll. Czech. Chem. Comm.*, 1951, **16–17**, 567.
[2] D. G. Davis, *Analyt. Chem.*, 1961, **33**, 492.
[3] C. Auerbach, H. L. Finston, G. Kissel and J. Glickstein, *ibid.*, 1961, **33**, 1480.
[4] M. T. Kelley, H. C. Jones and D. J. Fisher, *ibid.*, 1959, **31**, 1475.
[5] R. W. Schmid and C. N. Reilley, *J. Amer. Chem. Soc.*, 1958, **80**, 2087.
[6] R. L. Pecsok, *Analyt. Chem.*, 1953, **25**, 561.
[7] R. Přibil and B. Matyska, *Coll. Czech. Chem. Comm.*, 1951, **16–17**, 139.
[8] R. L. Pecsok and D. T. Sawyer, *J. Amer. Chem. Soc.*, 1956, **78**, 5496.
[9] J. H. Yoe, F. Will, III and R. A. Black, *Analyt. Chem.*, 1953, **25**, 1200.

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PROPERTIES OF BASES IN ACETONITRILE AS SOLVENT—III*

HYDROGEN BONDING BETWEEN PROTONATED AND FREE NITROGEN BASES

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Summary—In acetonitrile as solvent, the stronger nitrogen bases, *B*, form 1:1 and also higher hydrogen-bonded complexes with their conjugate acids, BH^+. Formation constants for these complexes have been determined by glass-electrode measurements in buffer solutions consisting of a constant concentration of the perchlorate or picrate of the base and varying concentrations of free base. The results show that the degree of complexation increases with increasing strength of the base and increasing number of hydrogen atoms in the ammonium group of the conjugate acid, and also that it has severe steric requirements, as expected. Thus, complexation is most extensive for the lower aliphatic primary amines and aliphatic cyclic secondary amines, such as piperidine, and does not occur with non-cyclic tertiary amines, except trimethylamine. The significance of these complexation reactions in potentiometric and conductimetric titrations and in studies concerned with the relative strength of bases is discussed.

INTRODUCTION

NON-AQUEOUS solvents have been used extensively in acid-base titrations, mainly in those cases where replacement of water by another solvent results in a desirable increase in solubility of the (organic) solutes, or improved sensitivity of the titration, or better differentiation of the components of mixtures, or where the use of a non-aqueous solvent avoids undesirable hydrolytic reactions. The subject has been thoroughly reviewed on several occasions by Riddick, and recently by Streuli.[1]

In the majority of cases the selection of solvent and titrant involved largely an empirical procedure of trial and error, because little theoretical information was available about the exact nature of the various solute species present and their interactions in these solvents. However, in recent years there has been an increasing interest in the theoretical aspects of acid-base reactions in non-aqueous solvents, particularly in solvents such as acetic acid and ethylenediamine, and in non-hydrogen bonding solvents of intermediate dielectric constant, such as the nitriles. Evidence is accumulating that probably no solvent is truly inert, and non-aqueous solvents provide a broad spectrum of conditions over which such solute-solvent interactions can be studied. However, certain non-aqueous solvents are much more inert in particular respects than water, and therefore provide suitable media for the investigation of the more subtle intrinsic properties of solutes, which are masked in water. Acetonitrile is such a solvent. It is a weaker base and a much weaker acid than water,

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* Part II: see reference 2.

and its dielectric constant is lower (36·0, as compared to 78·5 for water). The cumulative effect of these three factors is that acetonitrile is a much more differentiating solvent than water, as is reflected by its much smaller autoprotolysis constant (3×10^{-27}, as compared to 1×10^{-14} for water[2]). Nevertheless, the dielectric constant of acetonitrile is sufficiently high to allow extensive electrolytic dissociation of ionic solutes and to permit the study of such solutions by conductimetry and other electrometric methods.

An important consequence of the extremely weak acidic (hydrogen bonding) properties of acetonitrile is the fact that in solutions of many weak Brönsted acids, HA, the anions, A^-, are not stabilised sufficiently by solvation (which for the majority of anions must occur mainly by hydrogen bonding) and therefore resort to hydrogen bonding with undissociated acid instead, producing complexes such as $A^- \ldots HA$. Naturally, if such complexation reactions occur, the treatment of data obtained with hydrogen ion indicator electrodes, and by methods involving conductimetry, spectrophotometry, *etc.*, will be more complex than for the same solutes in water. The complexation reactions of Brönsted acids in acetonitrile have been studied thoroughly by Kolthoff and his coworkers.[3]

Analogous hydrogen bonded complexes between free and protonated amine-type bases are also produced in acetonitrile, although not to the same extent as for Brönsted acids. Nevertheless, some of these complexes are sufficiently stable to be important in acid-base titrations and particularly in theoretical studies concerned with the relative strength of bases. This communication is concerned with the formation of such complexes.

EXPERIMENTAL

Apparatus

Electromotive force measurements were made with a Beckman Model G pH meter and an *H*-type cell containing a Beckman "general purpose" No. 1190-80 glass electrode in conjunction with an Ag/(0·010M $AgNO_3$ in acetonitrile) reference electrode, and with 0·1M tetra-ethylammonium perchlorate in acetonitrile as salt bridge. This apparatus has been described elsewhere.[2]

Reagents

Technical grade acetonitrile (from two sources, Matheson and Sohio) was purified by a sequence of operations described before,[4] including fractional distillation, first from phosphorus pentoxide and then from calcium hydride.

The bases used were generally purified by distillation from sodium hydroxide and sodium metal (under reduced pressure for high-boiling bases). Full details will be presented elsewhere.[5] Boiling points agreed with literature values.

The perchlorates and picrates of the bases studied were generally prepared by potentiometric titration with the appropriate acid to the equivalence point (glass electrode) in water or ethanol as solvent, followed by evaporation of the solvent if necessary, and recrystallisation of the product from ethanol, isopropanol or ethyl acetate. Again, detailed information will be given elsewhere.[5]

RESULTS AND DISCUSSION

Cells containing glass electrodes in acetonitrile give a reversible response, provided the solutions are adequately buffered, a proper reference electrode is used, and liquid junction potentials are controlled, as described before.[2] For each base (B) studied, we have measured the potential of a glass electrode in a series of 8 to 14 buffer solutions consisting of a constant concentration ($C_s = 5 \times 10^{-4}M$) of the perchlorate or picrate of the base and varying concentrations (C_b) of free base. The salt concentration was deliberately kept low to minimise activity effects, changes in liquid junction potential and complications from $BH^+ClO_4^-$ and BH^+Pi^- ion pair formation, even though a higher concentration of salt would facilitate (qualitative) detection of $B{\cdot}BH^+$ and higher complexes.

For the dissociation of a protonated amine in a solvent *S* which has some proton acceptor power, the following equilibrium relationships apply:

$$BH^+_{\text{solvated}} + S \rightleftharpoons SH^+_{\text{solvated}} + B_{\text{solvated(?)}}$$

$$K_a = a_{SH^+} \cdot \frac{[B]}{[BH^+]} \cdot \frac{f_B}{f_{BH^+}}$$

where K_a is the thermodynamic dissociation constant of BH^+, and [X] denotes the molar concentration, a_X the activity and f_X the molar activity coefficient of species *X*. At constant ionic strength, f_B/f_{BH^+} is constant, so that

$$\frac{[B]}{[BH^+]} = \frac{\text{constant} \times K_a}{a_{SH^+}}.$$

If the electrode responds reversibly to a_{SH^+}, it follows from the Nernst equation that a plot of *E vs.* log ([B]/[BH^+]) or *vs.* log [B] at constant [BH^+], will be linear with a slope of 59 mV at 25°. If no complexation occurs between *B* and BH^+ and if the degree of dissociation of BH^+ is negligible compared to unity (as it is in all cases studied), [B] and [BH^+] are given by the total (analytical) concentrations C_b and C_s, respectively. However, if some BHB^+ formation occurs, it follows that

$$[B] = C_b - [BHB^+]$$

and

$$[BH^+] = C_s - [BHB^+]$$

so that a plot of *E vs.* log (C_b/C_s) will deviate from linearity. In the limiting case where formation of BHB^+ is virtually complete over the range of base concentrations studied, the plot will again be linear, but now with a slope of 118 mV.

In all cases formation constants of $B{\cdot}BH^+$ and $B_2{\cdot}BH^+$ complexes were evaluated from *E vs.* log (C_b/C_s) plots, such as those given in Figs. 1–4. In a relatively ideal case, such as that of piperidine (Fig. 2), only one complex (BHB^+) is produced and, furthermore, formation of this complex is virtually complete over a wide range of free base concentrations, so that calculation of the formation constant is straightforward. However, with the majority of bases studied the situation is more complicated, because either the species BHB^+ is insufficiently stable to be formed virtually exclusively even at the highest base concentrations studied (see below, pyridine), or else higher complexes such as $B_2{\cdot}BH^+$ (Fig. 1, n-butylamine) and even $B_4{\cdot}BH^+$ (Fig. 3, hydrazine) also are produced.

As an illustration of the calculations carried out, the case of pyridine will be considered. Pyridine forms a relatively weak complex $B{\cdot}BH^+$, and gives no evidence of forming higher complexes. Experimental data are given in Table I. For the last measurement listed, it follows from the Nernst equation that

$$\log\frac{0{\cdot}812 - x}{5 \times 10^{-4} - x} - \log\frac{0{\cdot}812}{5 \times 10^{-4}} = \frac{39}{59} = \log 4{\cdot}58$$

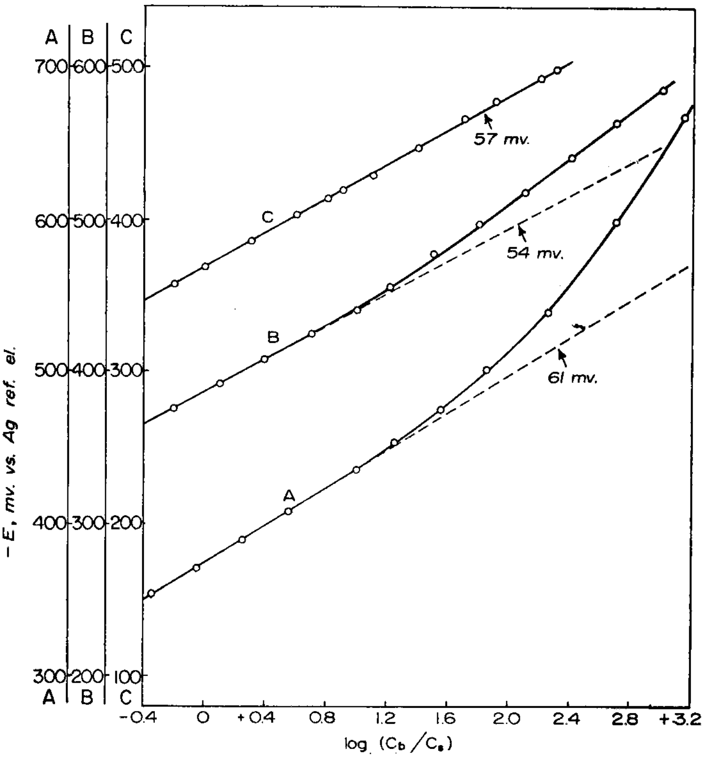


FIG. 1.—Potential of glass electrode in buffer solutions of n-butylamines and their perchlorates at a constant salt concentration of 5 × $10^{-4}M$: (*A*) n-Butylamine, (*B*) Di-n-butylamine, (*C*) Tri-n-butylamine.

where x represents the molar concentration of the BHB^+ complex. Hence,

$$\frac{0{\cdot}812 - \mathrm{x}}{5 \times 10^{-4} - \mathrm{x}} = 1624 \times 4{\cdot}58 = 7{\cdot}44 \times 10^3$$

so that

$$\mathrm{x} = [\mathrm{BHB^+}] = 3{\cdot}91 \times 10^{-4}$$

and

$$[\mathrm{BH^+}] = 5{\cdot}00 \times 10^{-4} - 3{\cdot}91 \times 10^{-4} = 1{\cdot}09 \times 10^{-4}.$$

Hence,

$$K = \frac{[\mathrm{BHB^+}]}{[\mathrm{B}][\mathrm{BH^+}]} = \frac{3{\cdot}91 \times 10^{-4}}{0{\cdot}812 \times 1{\cdot}09 \times 10^{-4}} = 4{\cdot}4.$$

Considering a more complicated example, that of n-butylamine, similar calculations give values of K that increase with increasing concentration of base: K = 26·3, 25·4, 32·2, 41·6 and 70·4 for C_b = 0·0174, 0·0348, 0·087, 0·261 and 0·696*M*, respectively. It is clear that (weak) higher complexes also are formed. In such cases the stepwise constants were computed by a series of approximations. For example, assuming as a first approximation that for n-butylamine $K_1 = 26$, it follows for the last measurement listed (C_b = 0·696*M*) that

$$[\mathrm{B{\cdot}BH^+}] = 26\,[\mathrm{B}][\mathrm{BH^+}].$$

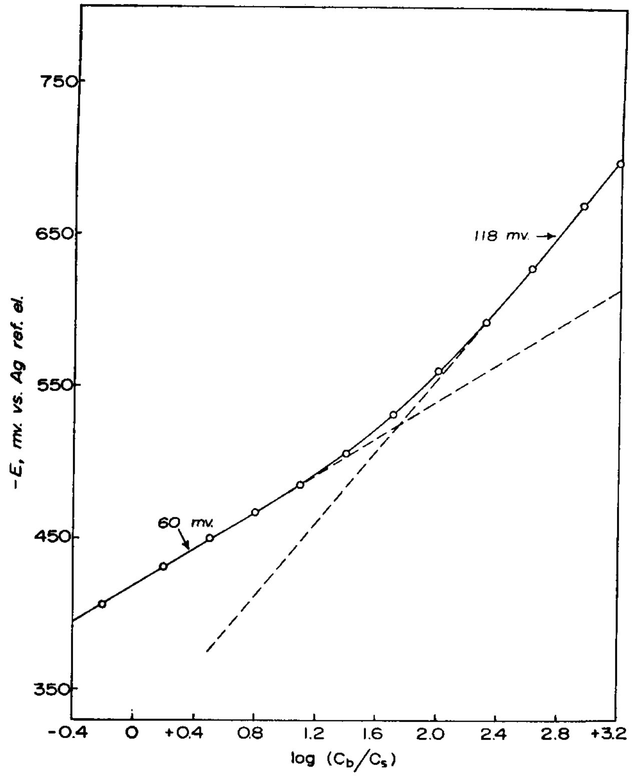


FIG. 2.—Glass electrode in piperidine-piperidinium picrate buffers at a constant salt concentration of 5 × $10^{-4}M$.

The value of $[BH^+]$ calculated as in the case of pyridine (*vide supra*) was found to be $1{\cdot}0 \times 10^{-5}$. Hence $[B{\cdot}BH^+] = 1{\cdot}81 \times 10^{-4}$, and

$$\begin{aligned}[B_2{\cdot}BH^+] &= C_s - [BH^+] - [B{\cdot}BH^+] \\ &= 5{\cdot}00 \times 10^{-4} - 1{\cdot}0 \times 10^{-5} - 1{\cdot}81 \times 10^{-4} \\ &= 3{\cdot}09 \times 10^{-4}\end{aligned}$$

so that

$$K_2 = \frac{[B_2{\cdot}BH^+]}{[B][B{\cdot}BH^+]} = \frac{3{\cdot}09 \times 10^{-4}}{0{\cdot}696 \times 1{\cdot}81 \times 10^{-4}} = 2{\cdot}5.$$

Similar calculations are carried out for all other points where formation of $B_2{\cdot}BH^+$ is apparent. For $C_b = 0{\cdot}261$ and $0{\cdot}087$, $K_2 = 2{\cdot}3$ and $2{\cdot}7$, respectively. The average value of K_2 (2·5) is then used to correct all preliminary values of K_1, which yields even for the last 3 measurements listed above a reasonably constant value of $K_1 = 26{\cdot}6$, 25·8 and 26·3, respectively. For cases where it was necessary, this sequence of calculations was repeated until (self-consistent) constant values of K_1 and K_2 were obtained. In the case of hydrazine (Fig. 3), where even higher complexes are also formed, an approximate value of K_2 was obtained by using the data for intermediate concentrations of base. Evaluation of K_3 and K_4 for hydrazine is too uncertain to be reported. More precise e.m.f. measurements (perhaps with a vibrating-reed electrometer as null detector) would be required for this purpose.

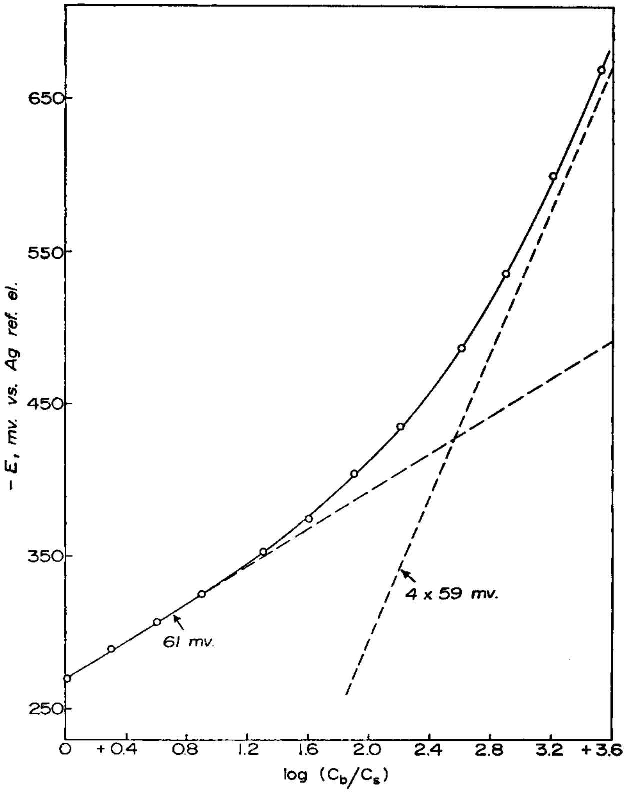


FIG. 3.—Glass electrode in hydrazine-hydrazonium monoperchlorate buffers at a constant salt concentration of 5 × $10^{-4}M$.

Formation constants for the complexes produced by a variety of nitrogen bases in acetonitrile as solvent are reported in Table II.

The main features of the results listed in Table II and in Figs. 1–4 are the following.

A. Non-cyclic aliphatic amines

1. The tendency of these amines to form 1:1 hydrogen bonded complexes, BHB^+, increases in the order tertiary, secondary, primary.

2. The tendency of the same amines to form higher complexes increases in the same order. Furthermore, it is to be expected that the highest complex that can be formed in any given case will be the species $B_n{\cdot}BH^+$, where n is the number of hydrogen atoms in the ammonium group and therefore represents the maximum number of hydrogen bonds that can be formed. The results are in agreement with this requirement.

3. However, steric factors are very important, as is most apparent from the behaviour of tertiary amines. Thus, while trimethylamine does form a 1:1 complex, triethylamine and its higher homologues form none. Similarly, the higher non-cyclic secondary amines do not form complexes.

B. Aromatic and cyclic aliphatic amines

1. The strength of the complex formed increases with increasing strength of the base. Thus, the relatively weak primary amines aniline and *p*-toluidine do not form

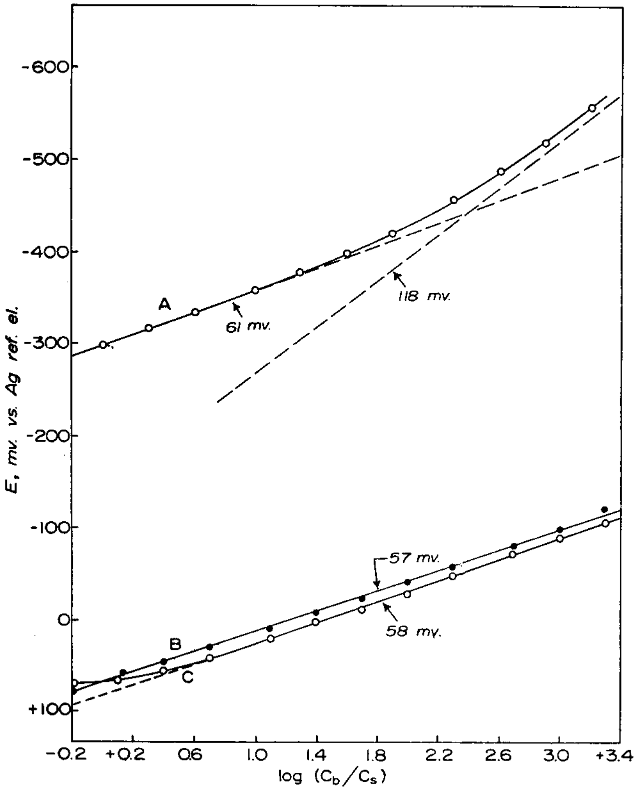


FIG. 4.—Glass electrode in benzylamine and aniline buffers at a constant salt concentration of $5 \times 10^{-4}M$:

(*A*) Benzylamine and its picrate, (*B*) Aniline and its perchlorate, (*C*) Aniline and its picrate.

TABLE I.—EXPERIMENTAL DATA FOR PYRIDINE

C_b*	ΔE, *mV*†	$[BHB^+] \times 10^4$	$[BH^+] \times 10^4$	K‡
0·101	11	1·75	3·25	5·3
0·125	11	1·75	3·25	4·3
0·250	17	2·43	2·57	3·8
0·304	22	2·88	2·12	4·5
0·500	27	3·26	1·74	3·8
0·812	39	3·91	1·09	4·4

* Total molar concentration of base added; concentration of salt (perchlorate) kept constant at $5{\cdot}00 \times 10^{-4}M$ for all 6 measurements.

† Difference from line of slope = 59 mV extrapolated from initial linear section of curve, which in the case of pyridine extended from the first point measured ($C_b = 2{\cdot}5 \times 10^{-4}M$) through the seventh ($C_b = 0{\cdot}020M$).

‡ Formation constant of BHB^+ complex. Omitting the first measurement, the average value is 4·2.

TABLE II.—FORMATION CONSTANTS OF HYDROGEN-BONDED COMPLEXES FORMED BETWEEN FREE AND PROTONATED BASES IN ACETONITRILE

Base	pK_a in water	Concn. range of base*		Salt	K_1†	K_2†
		Min., $M \times 10^4$	Max., $M \times 10$			
Ammonia	9·26	3	10	Perchlorate	11	2
Methylamine	10·64	3	11	Perchlorate	35	2
Dimethylamine	10·61	5	17	Perchlorate	31	0·5
Trimethylamine	10·72	2	2	Perchlorate	6	—
Ethylamine	10·75	4	8	Perchlorate	25	2
Diethylamine	11·00	4	7	Perchlorate	3	—
		5	8	Picrate	1	—
Triethylamine	10·74	1	1	Picrate	None	
n-Propylamine	10·59	3	8	Perchlorate	19	2
Tri-n-propylamine	10·70	3	0·8	Perchlorate	None	
n-Butylamine	10·61	2	7	Perchlorate	26·$_3$	2·$_5$
Di-n-butylamine	11·31	2	4	Picrate	None	
		2	5	Perchlorate	None	
Tri-n-butylamine	10·89	3	1	Perchlorate	None	
		2	0·8	Picrate	None	
t-Butylamine	10·45	2	8	Picrate	20	1
Di-isobutylamine	10·59	1	4	Picrate‡	None	
Tri-isoamylamine	—	4	0·7	Picrate‡	None	
Piperidine	11·20	2	9	Picrate	25·$_9$	—
Pyrrolidine	11·31	3	10	Picrate	33	2·$_5$
		3	9	Perchlorate	30	2
Pyridine	5·17	2	8	Perchlorate	4·$_2$	—
Aniline	4·58	3	11	Picrate	None	
		3	11	Perchlorate	None	
p-Toluidine	5·30	3	8	Perchlorate	None	
Benzylamine	9·30	3	9	Picrate	15	—
Monoethanolamine	9·45	3	8	Picrate	24	1·$_5$
Morpholine	8·36	3	10	Picrate	10	—
Hydrazine	7·99	4	12	Perchlorate	30	6§
Ethylenediamine	10·03	3	8	Perchlorate	40	1·$_5$
1,3-Propanediamine	10·64	3	8	Perchlorate	22	1·$_5$
1,4-Butanediamine	10·82	3	8	Perchlorate	10	1·$_5$
Triethylenediamine¶	8·19	3	8	Perchlorate	16	—

* Range over which total added base concentration was varied, while keeping salt concentration constant (at $5 \times 10^{-4}M$, except where indicated otherwise).

† K_1 and K_2 are stepwise formation constants:

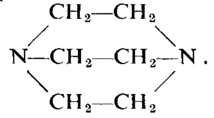
$$K_1 = \frac{[BHB^+]}{[B][BH^+]} \quad \text{and} \quad K_2 = \frac{[B_2BH^+]}{[B][BHB^+]}\,.$$

For diamines, the data refer to monoprotic species only.

‡ Salt concentration = $5 \times 10^{-2}M$.

§ Higher complexes, up to $B_4.BH^+$, also formed. Value of K_2 uncertain.

¶ Triethylenediamine:



complexes, while pyridine and especially benzylamine (Fig. 4) do. A similar correlation between the base strength and hydrogen bonding ability (acceptors: chloroform and methanol) has been observed with pyridines in the pure bases as solvent.[6]

2. The cyclic amines pyrrolidine and piperidine form complexes that are much more stable than those of the corresponding non-cyclic secondary amines. Similarly

the cyclic tertiary amine triethylenediamine (Table II) and even the relatively weak base pyridine form 1:1 complexes. Clearly, in these cases steric hindrance is less marked than for the corresponding non-cyclic amines.

C. Other generalisations

1. For the diamines, $H_2N{\cdot}(CH_2)_n{\cdot}NH_2$, BHB^+ formation decreases as n increases from 2 to 4, even though the base strength *increases* in this sequence (in both water and acetonitrile). In the cases where $n = 3$ and 4 internal hydrogen bonding (N—H . . . N) may stabilise the cation, thereby reducing its desire to form hydrogen bonds with free base. The diamines are an interesting series of compounds, exhibiting quite different relationships between hydrazine and the remaining members in acetonitrile and in water. These differences will be discussed elsewhere.[5]

2. Generally, the slopes of the *E vs.* log (C_b/C_s) plots in the early region, before complexation becomes significant, were within 1 or 2 mV from the theoretical value of 59 mV. However, in the case of di-n-butylamine (Fig. 1) the slope was considerably less (average of 4 series of measurements = 54 mV). The reason for this behaviour is unknown. In the case of aniline in picrate buffers (Fig. 4) there is marked curvature in the initial region of the plot. This is because of reversion of the salt to the weak parent acid and base:

$$BH^+ + Pi^- \rightleftharpoons B + HPi.$$

Titration curves

The complexation reactions of nitrogen bases in acetonitrile not only are interesting *per se*, but are also important in the interpretation of acid-base titration curves. Clearly, in the titration of an amine with perchloric acid the largest effect of complexation will occur in the early stages of the titration, and again just before the equivalence point, where either the base or the salt is in considerable excess over its conjugate species. It can be shown readily that complexation should result in a decrease of the buffer capacity of the solution and a reduction in the break at the equivalence point of a potentiometric titration. These generalisations were verified experimentally. For example, in a titration of 0·1 *M* pyrrolidine in acetonitrile with 0·5*M* perchloric acid dissolved in methylene chloride the potential of the glass electrode deviated from the hypothetical values calculated from the dissociation constant of pyrrolidinium ion in acetonitrile[5] on the assumption that no complexation, no ion pair formation and no interference by methylene chloride occurs, by −12, −5, +6 and +10 mV at 10, 30, 70 and 90% titrated, respectively, where negative values indicate that the solution is more basic than the hypothetical value, and *vice versa*. The formation constants reported for pyrrolidine (Table II) account for the major part of this variation.

The influence of complexation on the titration curves of amines with *weak* acids is more striking. Fig. 5 gives the conductimetric titration curves of n-butylamine with salicylic acid. The pronounced curvature before the equivalence point is from the BHB^+ complex (BH^+A^- ion pair formation is also important), and that after the equivalence point from the AHA^- complex (studied in detail for similar systems by Kolthoff and Chantooni[3]). In a masking solvent, such as water, the two branches of the curve are virtually linear, and the section after the equivalence point is nearly horizontal. We will discuss elsewhere the conductimetric titration curves of a variety of amines with *ortho*-substituted benzoic acids.

CONCLUSIONS

It has been shown that many of the stronger amines, particularly aliphatic primary and cyclic secondary amines, form hydrogen-bonded complexes with their conjugate acids in acetonitrile as solvent. One may speculate that this behaviour is likely to be the norm, rather than the exception, in the majority of solvents which have very weak-base properties. A formation constant near 30, which is typical for a number of these bases in acetonitrile, corresponds to a free energy of formation given by

$$\Delta F = -10^{-3}\,RT \ln K = -10^{-3} \times 2{\cdot}0 \times 298 \times 2{\cdot}3 \times 1{\cdot}48 = -2{\cdot}0 \text{ kcal/mole.}$$

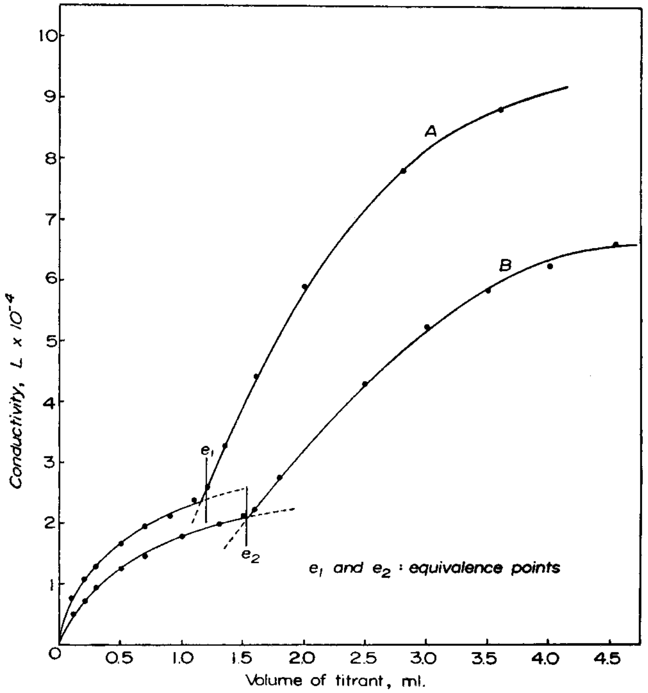


FIG. 5.—Conductimetric titration of n-butylamine with salicylic acid:
(*A*) 0·0287*M* base with 0·478*M* acid,
(*B*) 0·0191*M* base with 0·249*M* acid.

The corresponding complexes, AHA^-, formed between a number of Brönsted acids and their anions[3] are more stable, with formation constants ranging up to 10^3, corresponding to $\Delta F = -4$ kcal/mole. This difference reflects the fact that acetonitrile is more reluctant to solvate anions than cations, as compared to analogous solvation by water.

It is necessary to consider the possible formation of BHB^+ complexes in any exact determination of the relative strength of amines (with the proton as reference acid) in acetonitrile and similar solvents. If the potential of a hydrogen-ion indicator electrode at the "half-neutralisation" point in the titration of an amine with a relatively strong acid is regarded as an index of the strength of the base,[7] an error will be introduced if complexes higher than the 1:1 species are produced. We have determined the pK_a values of a series of nitrogen bases in acetonitrile by measurements similar to those described in this communication, but with provisions to maintain the absolute value of the net liquid junction potential constant for the entire series, and by making due allowance for complexation reactions. The results will be presented elsewhere.[5]

Acknowledgments—We thank the National Science Foundation for financial support under grant number NSF-G14502. We also wish to express our indebtedness to Professor Kolthoff, whose classical investigations of many facets of the chemistry of non-aqueous solutions have created widespread interest in this field.

Zusammenfassung—In Acetonitril als Lösungsmittel bilden stärkere Stickstoffbasen B mit einem oder mehreren Molekülen ihrer konjugierten Säuren BH^+ Wasserstoffbrückenkomplexe. Bildungskonstanten solcher Komplexe wurden durch Messungen mit Glaselektroden in Pufferlösungen aus konstanten Mengen des Perchlorats oder Pikrats der Base und variablen Mengen der freien Base bestimmt. Die Ergebnisse zeigen, daß der Komplexbildungsgrad mit steigender Basenstärke und steigender Anzahl von Wasserstoffatomen in der Ammoniumgruppe der konjugierten Säure wächst. Ferner sind erwartungsgemäß strenge sterische Bedingungen zu erfüllen. So ist die Komplexbildung am stärksten bei den niedrigen aliphatischen primären und den cyclischen sekundären Aminen wie Piperidin und bleibt bei nichtcyclischen tertiären Aminen außer Trimethylamin überhaupt aus. Die Bedeutung dieser Komplexbildungsreaktionen bei potentiometrischen und konduktometrischen Titrationen und bei Untersuchungen über die relative Stärke von Basen wird diskutiert.

Résumé—Dans l'acétonitrile, les bases fortes azotées, B, forme des complexes 1/1 et plus élevée par liaison hydrogène avec leurs acides conjugués BH^+. Les constantes de formation des ces complexes ont été déterminées par mesure au moyen d'électrode de verre en solution tamponnées constituées par un perchlorate ou un picrate de la base étudiée en concentration constante et en présence de concentrations variables de base libre. Les résultats montrent que le taux de complexation augmente avec l'accroissement de la force de la base et avec le nombre d'atomes d'hydrogène du groupement ammonium dans l'acide conjugué, et également que les impératifs stériques jouent un grand rôle, comme il faut s'y attendre. Ainsi, la formation de complexe est plus accentuée pour les amines aliphatiques primaires lègères et les amines secondaires aliphatiques cycliques, comme la pipéridine, et n'apparaît pas avec les amines tertiaires non-cycliques, excepté la triméthylamine. Discussion de la signification de ces réactions de formation de complexes dans les dosages par potentiométrie et conductimétrie et dans les études relatives aux diverses forces de ces bases.

REFERENCES

[1] J. A. Riddick, *Analyt. Chem.*, 1960, **32**, 172 R; C. A. Streuli, *ibid.*, 1962, **34**, 302 R.
[2] J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, 1962, **66**, 1708.
[3] I. M. Kolthoff, S. Bruckenstein and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, 1961, **83**, 3927; I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, 1963, **85**, 426.
[4] J. F. Coetzee, G. P. Cunningham, D. K. McGuire and G. R. Padmanabhan, *Analyt. Chem.*, 1962, **34**, 1139.
[5] J. F. Coetzee and G. R. Padmanabhan, to be published.
[6] M. Tamres, S. Searles, E. M. Leighly and E. W. Mohrman, *J. Amer. Chem. Soc.*, 1954, **76**, 3983.
[7] H. K. Hall, Jr., *J. Phys. Chem.*, 1956, **60**, 63.

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A.C. POLAROGRAPHIC STUDIES ON THE INFLUENCE OF TENSAMMETRIC WAVES ON REDUCTION PEAKS OF INORGANIC CATIONS AND *VICE VERSA*

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Summary—This investigation deals with the studies on the effect of the nature and concentration of surface active substances (s.a.s) on the a.c. reduction peaks of Cd^{2+} and Zn^{2+} ions and *vice-versa* by a.c. polarography. The magnitude of the reduction peak is not influenced up to a certain concentration of the s.a.s., but with concentrations higher than this, the magnitude of the reduction peak progressively decreases; a concentration of 1·3% of n-amyl alcohol completely removes the $10^{-3}M$ Cd^{2+} peak. Neither magnitude nor the peak potential of the tensammetric peak of n-amyl alcohol are influenced by the presence of Cd^{2+} ions. There is a linear relation between the concentration of the electroactive species and the optimum concentration of the s.a.s., and also the concentration of the s.a.s. just required to remove the reduction peak. These observations are further supported by the curve which gives the linear relation between the concentration of the electroactive species and the amount of the s.a.s. required to reduce the magnitude of the reduction peak to half its value. The amount of the surfactants required to remove the reduction peak completely is in the order n-amyl alcohol > Cerfak [sodium napthalene (2-dodecyl)3-sulphonate] > cetylpyridinium bromide. These results are discussed.

INTRODUCTION

SURFACE active substances usually employed to eliminate maxima on polarographic waves often cause undesirable effects such as suppression of a diffusion current, shift of a half-wave potential, splitting of a wave into two or more waves; in some cases the entire wave is obliterated, or a combination of these effects occurs. Breyer and Hacobian[1] studied the influence of tensammetric waves on a.c. and d.c. polarography. They showed, however, that in the presence of cyclohexanol the discharge of Cd^{2+} ions was rendered irreversible, as shown by the absence of an a.c. polarogram, only the tensammetric wave of cyclohexanol appearing. In contradistinction to Cd^{2+} the discharge of Mn^{2+} (−1·5v *vs.* S.C.E.) was completely unaffected by the presence of cyclohexanol.

The purpose of the present investigation was to study in detail the effect of the nature and concentration of surface active substances, *viz.*, n-amyl alcohol, Cerfak [sodium napthalene(2-dodecycl)3-sulphonate] and cetylpyridinium bromide, on the a.c. reduction peaks of Cd^{2+} and Zn^{2+} ions and *vice versa*. It is also to be seen if there is a possible correlation between the optimum concentration of the surface active substance and the amount of reducible species before any of the above undesirable effects are operative was also sought. This would be of great significance in removing polarographic maxima in d.c. polarography.

EXPERIMENTAL

Reagents

Cadmium sulphate and *zinc sulphate* used as reducible species were AnalaR quality (B.D.H.) *Normal amyl alcohol* of "Baker analysed reagent grade" was used as non-ionic surface active substance Pure samples of *Cerfak* and *cetylpyridinium bromide* were used as anionic and cationic agents respectively. All other chemicals used were of analytical quality, B.D.H.

Mercury used for the pool and the dropping electrode was passed through a Meyer's column[2] washed several times with distilled water, dried, passed through a sintered-glass filter and finally distilled under vacuum.

Apparatus

The apparatus employed in the present investigation is the same as that described before,[3,4] the only modification being as much reduction as possible of series resistance. This is done by applying to a dropping mercury electrode a 50-cycle a.c. ripple of 40 mV (r.m.s.) over the d.c. potentials and observing the alternating component of the resulting pulsating current. The d.c. potentials have been expressed with reference to the saturated calomel electrode. The constants of the d.m.e were as follows.

$m = 3{\cdot}559$ mg per sec.

$t = 2{\cdot}3$ sec per drop in $0{\cdot}1M$ KCl (open circuit).

Potassium chloride solution ($0{\cdot}1M$) was used as the supporting electrolyte, and was invariably shaken and kept in contact with mercury and mercurous chloride. In each case the measurements were taken with the indifferent electrolyte, and the effect has been expressed in terms of the per cent increase (with sign) of the alternating current. The d.m.e. was cathodic throughout the measurements. All the experiments were done at a pH of 3·3 and a temperature of 30 ± 0·5°.

RESULTS

Fig. 1 shows the effect of various concentrations of n-amyl alcohol on the Cd^{2+} ($10^{-3}M$)reduction peak. It is seen, in general, that the magnitude of the reduction peak is not influenced up to a certain concentration, known as the optimum concentration of the s.a.s., but with concentrations higher than this the magnitude of the reduction peak progressively decreases, so much so that a concentration of 1·3% of n-amyl alcohol completely removes the $10^{-3}M$ Cd^{2+} peak. The magnitude and the peak potential of the tensammetric peak of n-amyl alcohol shows the normal behaviour that would be expected without the presence of Cd^{2+} ions. These observations are further supported by Fig. 2, which gives the effect of various concentrations of Cerfak on the $10^{-3}M$ Cd^{2+} reduction peak. In this case, 0·066% of Cerfak is sufficient to remove the Cd^{2+} peak completely.

Fig. 3 shows the effect of various concentrations of Cd^{2+} ions on the tensammetric peak of 1·3% n-amyl alcohol. It is again confirmed that the $10^{-3}M$ Cd^{2+} peak is completely suppressed by 1·3% n-amyl alcohol, whereas, with higher concentrations of Cd^{2+}, the reduction peak reappears; its magnitude then increases with increase in the concentration of Cd^{2+} ion without affecting either the magnitude or the peak potential of the tensammetric peak of 1·3% n-amyl alcohol.

Fig. 4 gives the curve which relates the amounts of n-amyl alcohol required just to remove the Cd^{2+} peak completely using different concentrations of the electroactive species. It can be seen that the curve is linear within the concentration range $10^{-4}M$–$10^{-3}M$ of the electroactive species. From this curve one can see directly the amount of s.a.s. just required to remove completely the reduction peak of an electroactive species corresponding to any particular concentration. In other words, it gives the concentration of the s.a.s. which is sufficient to make the discharge process completely irreversible.

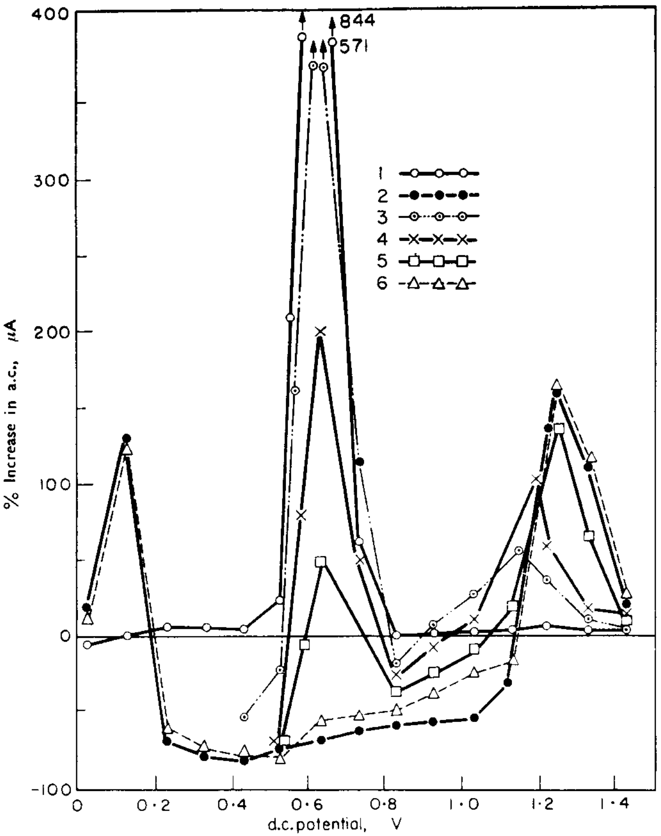

Fig. 1.—The effect of various concentrations of n-amyl alcohol on the Cd^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Cd^{2+}
2. 1·3% n-amyl alcohol
3. $10^{-3}M$ Cd^{2+} + 0·4% n-amyl alcohol
4. $10^{-3}M$ Cd^{2+} + 0·7% n-amyl alcohol
5. $10^{-3}M$ Cd^{2+} + 1·0% n-amyl alcohol
6. $10^{-3}M$ Cd^{2+} + 1·3% n-amyl alcohol.

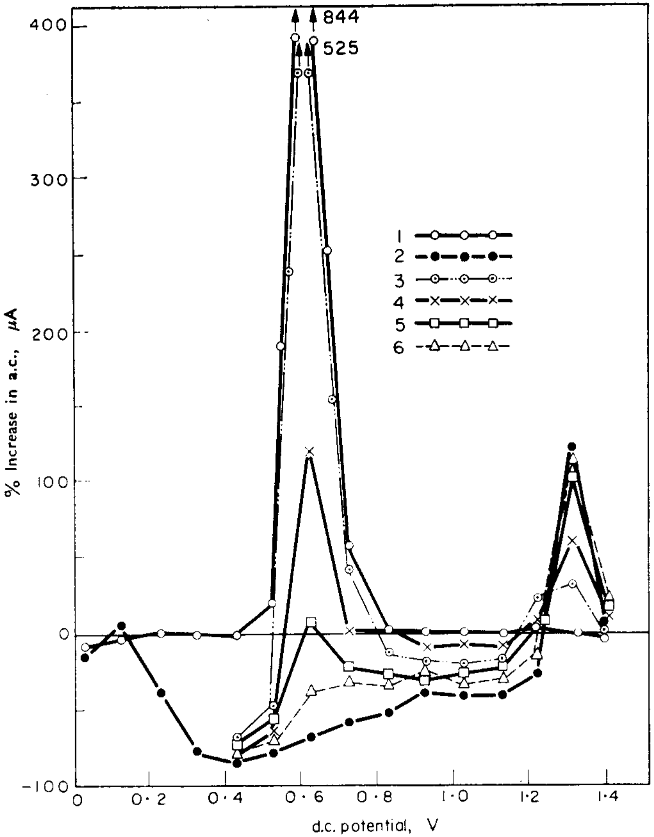

Fig. 2.—The effect of various concentrations of Cerfak on the Cd^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Cd^{2+}
2. 0·066% Cerfak
3. $10^{-3}M$ Cd^{2+} + 0·02% Cerfak
4. $10^{-3}M$ Cd^{2+} + 0·04% Cerfak
5. $10^{-3}M$ Cd^{2+} + 0·06% Cerfak
6. $10^{-3}M$ Cd^{2+} + 0·066% Cerfak.

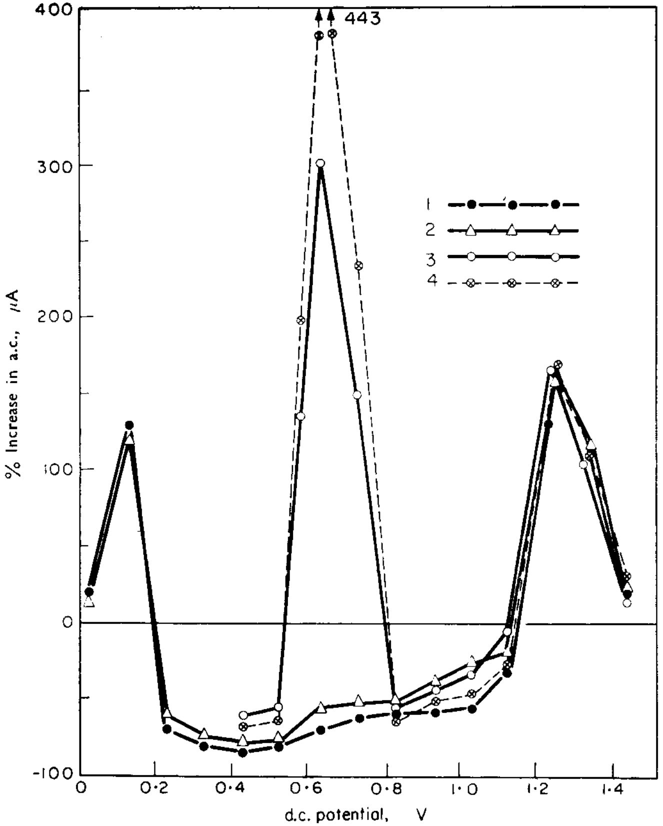

FIG. 3.—The effect of various concentrations of Cd^{2+} ion on the tensammetric peak of 1·3% n-amyl alcohol.

1. 1·3% n-amyl alcohol
2. 1·3% n-amyl alcohol + $10^{-3}M$ Cd^{2+}
3. 1·3% n-amyl alcohol + 3 × $10^{-3}M$ Cd^{2+}
4. 1·3% n-amyl alcohol + 5 × $10^{-3}M$ Cd^{2+}.

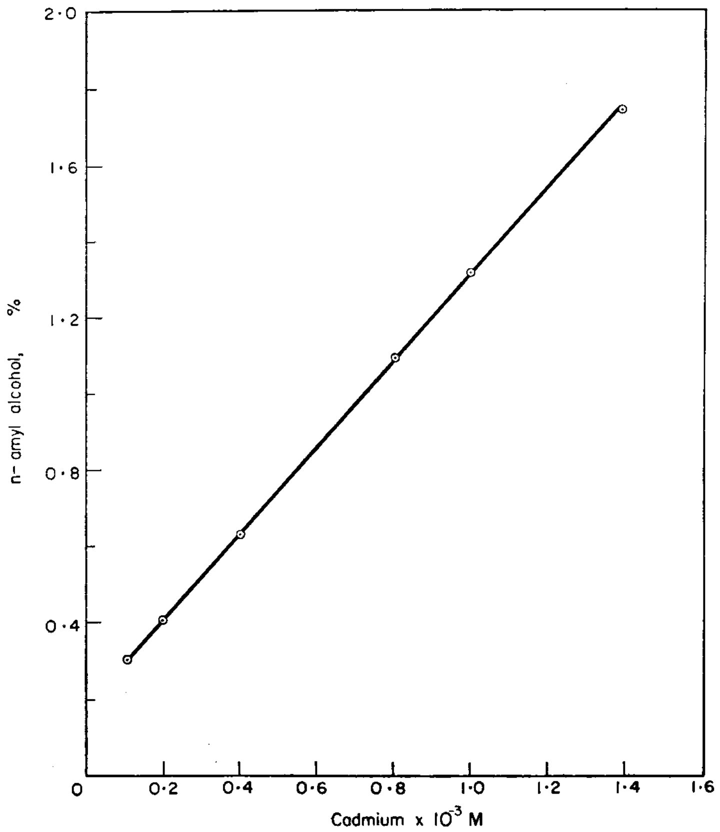

FIG. 4.—Relation between the amounts of n-amyl alcohol required to remove the Cd^{2+} peaks completely for various concentrations of Cd^{2+} ion.

Fig. 5 relates the optimum concentrations of n-amyl alcohol used for various concentrations of Cd^{2+} ion to produce the reduction peak. Here again it can be seen that the relation is linear in the concentration range $10^{-4}M$–$10^{-3}M$ of Cd^{2+}. This relation should be of particular interest in connection with d.c. polarography, where the optimum concentration of the s.a.s. is of significance in suppressing the polarographic maxima.

These observations are further substantiated by Fig. 6, which shows the linear relation between the concentration of the electroactive species and that of the surface active substance required to reduce the magnitude of the reduction peak to half its value. This linear relation holds good for the electroactive species between $10^{-4}M$ and $10^{-3}M$. The relation between the magnitude of the reduction peak and the molar concentration of the Cd^{2+} ion is linear within the above range.[5]

Fig. 7 shows the effect of various concentrations of n-amyl alcohol on the reduction peak of $10^{-3}M$ Zn^{2+} ions. Here, also, as in the case of Cd^{2+} ions, up to a certain concentration of n-amyl alcohol, the magnitude of the Zn^{2+} peak is not affected at all; but with concentrations greater than this optimum concentration, the magnitude of the peak decreases progressively till it is completely removed by 1·0% n-amyl alcohol. Further, the peak potential and the magnitude of the tensammetric peak of 1·0% n-amyl alcohol remain unaffected by the presence of $10^{-3}M$ Zn^{2+} ions.

These observations are further confirmed by Fig. 8 and Fig. 9, which show the effect of various concentrations of Cerfak and cetylpyridinium bromide on the reduction peaks of $10^{-3}M$ Zn^{2+} ion. The concentrations of Cerfak and cetylpyridinium bromide required for completely removing the reduction peak are 0·056% and 0·008%, respectively. Therefore to remove completely the reduction peak of $10^{-3}M$ Zn^{2+}, the quantities of s.a.s. required are in the order n-amyl alcohol > Cerfak > cetylpyridinium bromide; this is supported by the effect of these s.a.s. on the reduction peak of Cd^{2+} ion.

DISCUSSION

Tensammetric peaks[1] are the outcome of the electrode processes which have their origin in adsorption/desorption processes occurring at the d.m.e. when a small sinusoidal a.c. voltage is superimposed upon the direct potential applied to a d.m.e. in the presence of s.a.s. and the resultant a.c. current is measured. They differ fundamentally from the a.c. reduction peaks of inorganic cations which are produced as a consequence of depolarisation processes occurring at the d.m.e., in the sense that in the former case no electron transfer takes place across the electrode boundary, whereas in the latter case it does.

In the absence of s.a.s. the reduction of inorganic cations takes place unhindered at the d.m.e. at the corresponding peak potential, and gives very high peaks which are reversible and diffusion-controlled. If s.a.s. is added, by virtue of the hydrophobic groups in the molecule it is preferentially adsorbed on the electrode surface, and hinders the electrode process either by film formation or by chemical interaction with the electroactive species in the immediate vicinity of the electrode surface. This adsorption is maximum at the electrocapillary zero (e.c.z), and diminishes on either side of the e.c.z. giving rise to tensammetric peaks arising from sudden desorption of the s.a.s. at higher cathodic or anodic potentials. It is obvious, therefore, that the electrode processes whose reduction potentials lie within the adsorption range of the

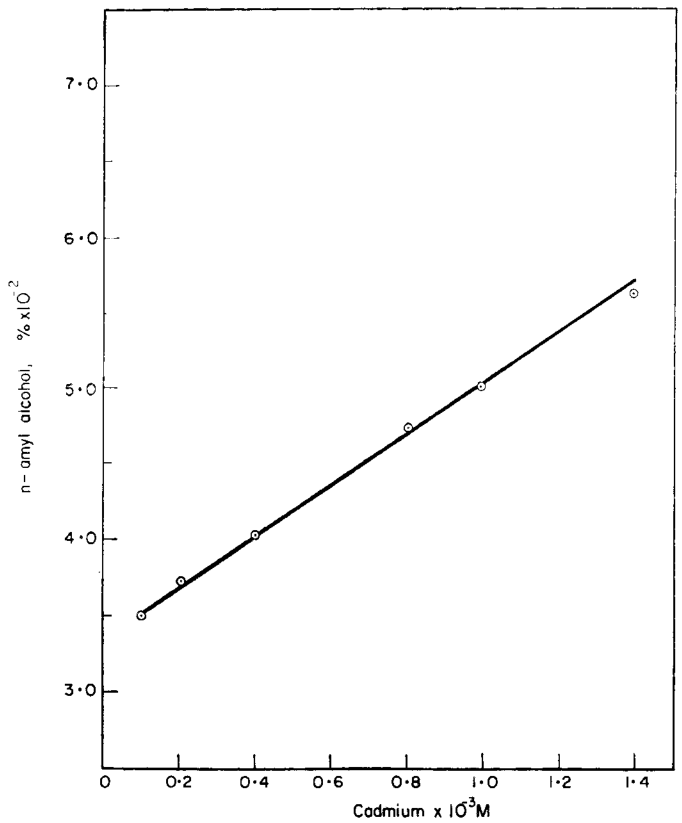

FIG. 5.—Relation between the optimum concentrations of n-amyl alcohol required, for various concentrations of Cd^{2+} ion.

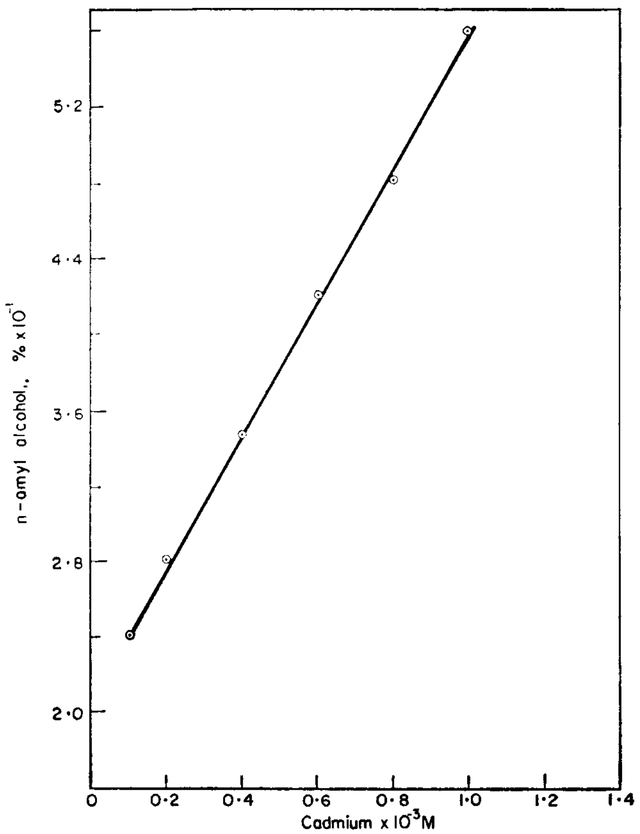

FIG. 6.—Relation between the concentrations of Cd^{2+} ion and n-amyl alcohol required to reduce the magnitude of the reduction peak to half its value.

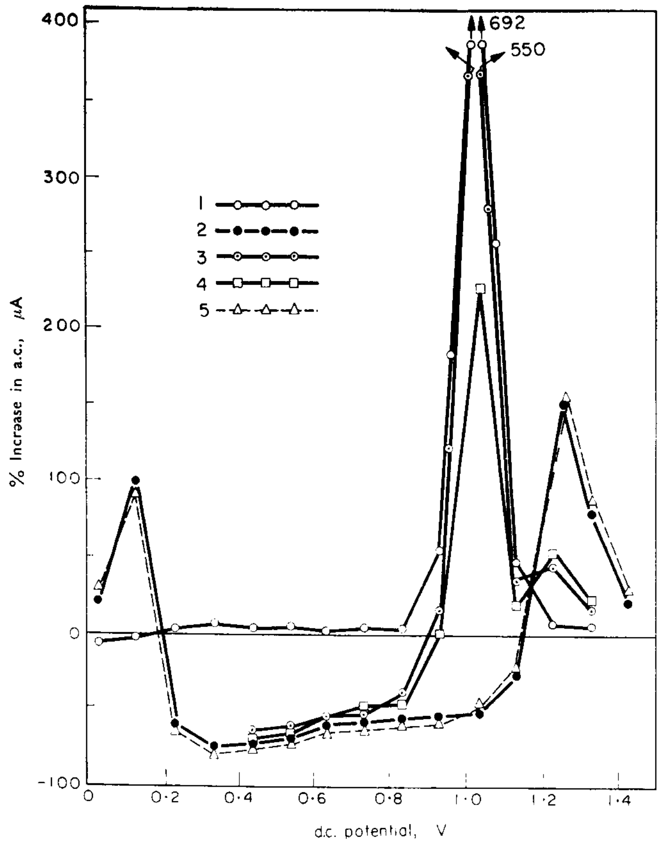

FIG. 7.—The effect of various concentrations of n-amyl alcohol on the Zn^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Zn^{2+}
2. 1·0% n-amyl alcohol
3. $10^{-3}M$ Zn^{2+} + 0·2% n-amyl alcohol
4. $10^{-3}M$ Zn^{2+} + 0·4% n-amyl alcohol
5. $10^{-3}M$ Zn^{2+} + 1·0% n-amyl alcohol.

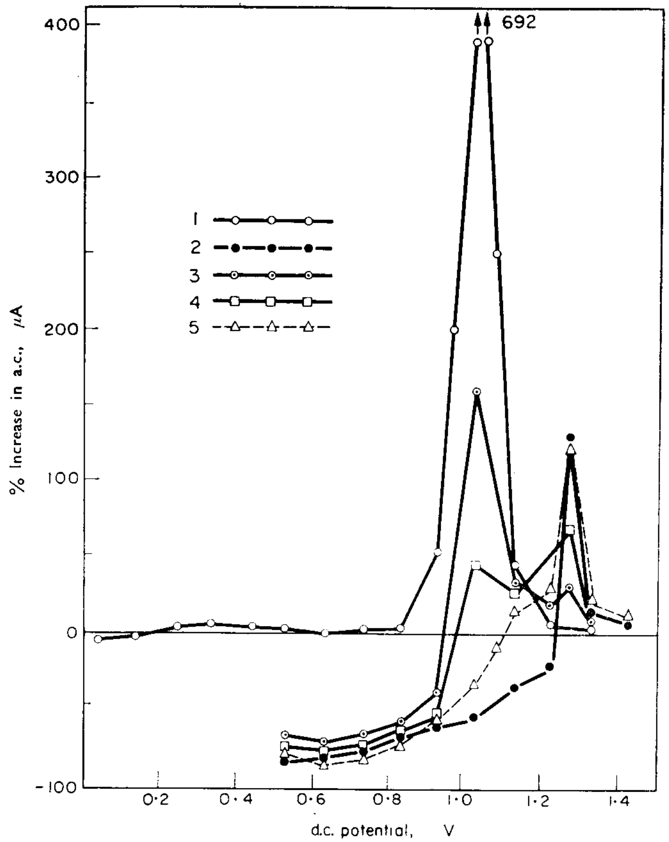

FIG. 8.—The effect of various concentrations of Cerfak on the Zn^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Zn^{2+}
2. 0·056% Cerfak
3. $10^{-3}M$ Zn^{2+} + 0·02% Cerfak
4. $10^{-3}M$ Zn^{2+} + 0·04% Cerfak
5. $10^{-3}M$ Zn^{2+} + 0·056% Cerfak.

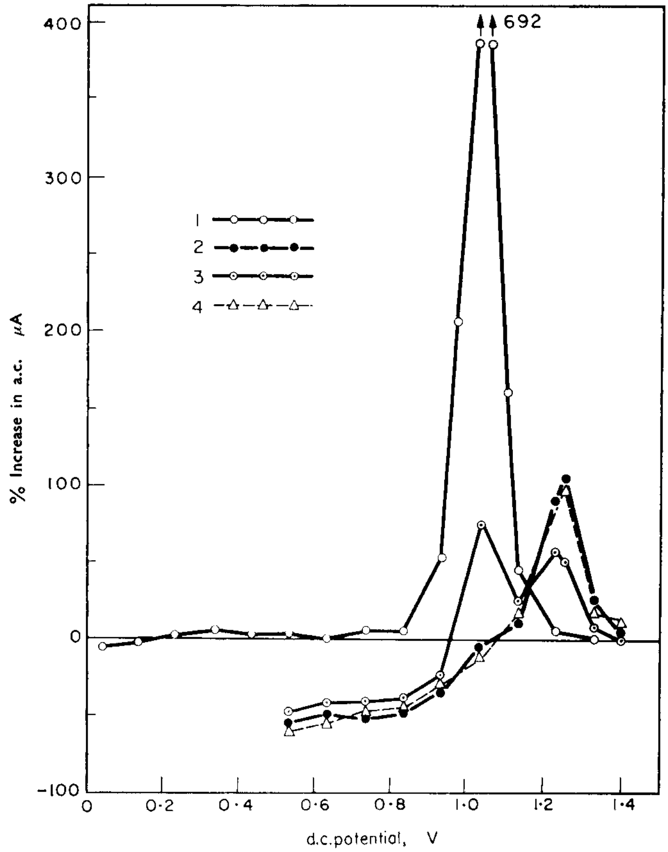

FIG. 9.—The effect of various concentrations of cetylpyridinium bromide on the Zn^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Zn^{2+}
2. 0·008% cetylpyridinium bromide
3. $10^{-3}M$ Zn^{2+} + 0·004% cetylpyridinium bromide
4. $10^{-3}M$ Zn^{2+} + 0·008% cetylpyridinium bromide.

s.a.s. will be affected by the presence of s.a.s., whereas outside this range there will be no significant influence on the electrode processes.

Because the peak potential and the magnitude of the tensammetric peak corresponding to any particular amount of s.a.s. remain constant with and without electroactive species, this suggests that the hindrance of the electrode process probably arises from film formation at the electrode surface and not from any chemical interaction between s.a.s. and the electroactive speices. This is further supported by Fig. 3, in which both the peak potential and the amount of 1·3% n-amyl alcohol are unaffected by adding various amount of Cd^{2+} ions in the solution . It appears that with concentrations up to the optimum concentration of the s.a.s., the amount of s.a.s. is not sufficient to cover the electrode surface to a sufficient extent to hinder the electrode process, but concentrations greater than the optimum concentration progressively increase the extent of surface coverage within the life of the drop, and increase the degree of hindrance of the electrode process, thereby diminishing the magnitude of the reduction peak. At higher concentrations of the s.a.s., corresponding to the removal of the reduction peak, it appears that most of the surface is covered with a unimolecular film; this hinders the rate of electron transfer from the electrode surface so much that it becomes slower than the diffusion rate, and hence the limiting current is no longer diffusion controlled. Thus a decrease in the rate of the electron transfer corresponds to an increase in irreversilibity of the electrode reaction, thereby producing no peak in a.c. polarography.

With larger amounts of a particular reducible species, the quantity of the s.a.s. needed to make the rate of electron transfer slower than the rate of diffusion will be more than when smaller amounts of the same reducible species are present. Hence it is seen that the amount of n-amyl alcohol required for removing the reduction peak of Cd^{2+} using larger concentrations of Cd^{2+} ions are more than those for smaller amounts of Cd^{2+} ions. It may be mentioned that although the concentration of surfactants below the optimum concentration do not show any adverse effects on the kinetics of the electrode process, they are nevertheless capable of suppressing the polarographic maxima, probably because of preferential adsorption of the s.a.s. at the neck of the mercury drop.[6]

The extent of inhibition on the kinetics of the electrode process depends, amongst other factors, on the structure of the adsorbed film, which in turn depends both on the nature of the s.a.s., especially its charge, and on the nature of the reducible species. On the cathodic side of the e.c.z., cationic surfactants will be adsorbed more strongly than anionic surfactants, and therefore the amount of cetylpyridinium bromide (which is cationic) required to remove Cd^{2+} and Zn^{2+} peaks is much less than the amount of Cerfak (which is anionic in nature.)

Acknowledgment—The authors are thankful to the C.S.I.R, New Delhi, for the award of fellowship to one of them (S. K. S).

Zusammenfassung—Diese Arbeit befaßt sich mit dem Effekt von Art und Konzentration oberflächenaktiver Stoffe auf die Wechselstromreduktionsspitzen von Cd^{2+} und Zn^{2+} in der Wechselstrompolarograp hiesowie den umgekehrten Effekten. Die Größe der Reduktionsspitze wird bis zu einer gewissen Konzentration des oberflächenaktiven Stoffes nicht beeinflußt, darüber nimmt die Spitze ab; eine Konzentration von 1,3% n-Amylalkohol unterdrückt die Spitze bei 10^{-3}m Cd^{2+} ganz. Größe und Potential der tensammetrischen Spitze von n-Amylalkohol werden durch Cd^{2+} nicht beeinflußt. Es besteht eine lineare Beziehung zwischen der Konzentration des reduzierbaren Ions und der Optimalkonzentration des oberflächenaktiven Stoffes und der Konzentration, die zur Unterdrückung der Spitze eben ausreicht. Diese Beobachtungen werden weiter gestüzt durch die lineare Beziehung zwischen Konzentration des reduzierbaren Ions und der Menge des oberflächenaktiven Stoffes, die die Größe der Spitze halbiert. Die zur völligen Unterdrückung der Reduktionsspitze notwendige Menge oberflächenaktiven Stoffes fällt von n-Amylalkohol über Cerfak zu Cetylpyridiniumbromid. Diese Ergebnisse werden in dieser Arbeit diskutiert.

Résumé—Cette recherche traite des études sur l'effet de la nature et de la concentration des substances tensioactives (s.t.a.) sur les pics de réduction en c.a. des ions Cd^{2+} et Zn^{2+} et vice-versa par polarographie en c.a. On voit que l'amplitude du pic de réduction n'est pas influencée jusqu'à une certaine concentration en s.t.a., mais à des concentrations supérieures à celle-ci, l'amplitude du pic de réduction décroît progressivement de sorte qu'une concentration de 1,3% en alcool n-amylique supprime complètement le pic 10^{-3}M Cd^{2+}. L'amplitude, ainsi que le potentiel de pic du pic tensammétrique de l'alcool n-amylique ne sont pas influencés par la présence d'ions Cd^{2+}. Il y a une relation linéaire entre la concentration de l'espèce électroactive d'une part, et la concentration optimale de la s.t.a., ou les concentrations de s.t.a. juste nécessaires pour annuler le pic de réduction d'autre part. Ces observations sont en outre étayées par la courbe qui donne la relation linéaire entre la concentration de l'espèce électroactive et la quantité de s.t.a. nécessaire pour diminuer de moitié l'amplitude du pic de réduction. La quantité de surfactant nécessaire pour supprimer totalement le pic de réduction se classe dans l'ordre: alcool n-amylique > cerfak > bromure de cétylpyridinium. Ces résultats sont discutés dans le mémoire.

REFERENCES

[1] B. Breyer and S. Hacobian, *Austl. J. Sci. Res.*, A, 1952, 5, 500.
[2] L. Meyer, *Chem.*, 1863, 2, 241.
[3] K. S. G. Doss and A. Kalyanasundaram, *Proc. Indian Acad. Sci.*, 1952, **35**, 27.
[4] K. S. G. Doss and S. L. Gupta, *ibid*, 1952, 36, 493.
[5] N. A. Ramaiah and S. K. D. Agarwal, *ibid.*, 1956, **54**, 26.
[6] P. Zuman and I. M. Kolthoff, *Progress in Polarography* Vol. I. Interscience, New York, 1962. p. 84.

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SOME TEMPERATURE EFFECTS IN GAS CHROMATOGRAPHY

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Summary—The expected effects of temperature on column efficiency are considered in detail for typical compounds of low, intermediate and high retention. Situations involving various relative values of the resistances to mass transfer in the gas and liquid phases are analysed. One conclusion reached is that flow conditions cannot be chosen at any one temperature which will result in maximum efficiency for all solutes. It would also be expected that column efficiency generally should increase with increasing temperature although under some conditions, of high mass transfer resistances in the liquid phase relative to that in the gas phase, a decrease or virtual independence of temperature may be found. The effect of variation of column temperature on pressure drop across the column is also examined briefly.

THE early work of Van Deemter *et al.*[1] immediately led to a greater understanding of the theory and practice of gas chromatography. Significant progress has been made with regard to theory since then by a number of persons of whom Jones,[2] Giddings[3] and Golay[4] might be mentioned. Much of the effort has been in relation to isothermal chromatography. It has been shown[5] that a knowledge of isothermal behaviour is important to an understanding of programmed temperature gas chromatography. In this paper some of the effects of temperature on isothermal gas chromatography, particularly with respect to column efficiency are examined. Because column efficiency is intimately related to the flow rate of the eluent gas and the distribution coefficients of the sample components, the effect of temperature on these two variables will first be briefly considered.

Flow rate and pressure drop

The effect of temperature on flow rate is primarily through its influence on gas viscosity which relates the flow rate to the pressure drop. There is a further strong effect from direct gas expansion if comparisons are made for conditions of constant mass flow rate.

The viscosity of most gases at ordinary pressures is approximately proportional to the temperature raised to a power somewhat less than one.[6] At high temperatures the limiting value of the slope shows a temperature dependence to the 0·63-power. At lower temperatures the coefficient is somewhat larger and no great error is incurred if the viscosities of gases of chromatographic interest are assumed to vary as the 0·7-power of the temperature.

It is noteworthy that the viscosity of hydrogen is about $0{\cdot}84 \times 10^{-4}$ g/sec. cm at 0° and 1 atmos, whereas all other gases of chromatographic interest have viscosities which are about twice this value. Therefore, the absolute change in viscosity with temperature as well as the viscosity itself is least for hydrogen. Thus hydrogen is unquestionably the preferred eluent gas, both from the point of view of minimum pressure drop and of least change in pressure drop with temperature.

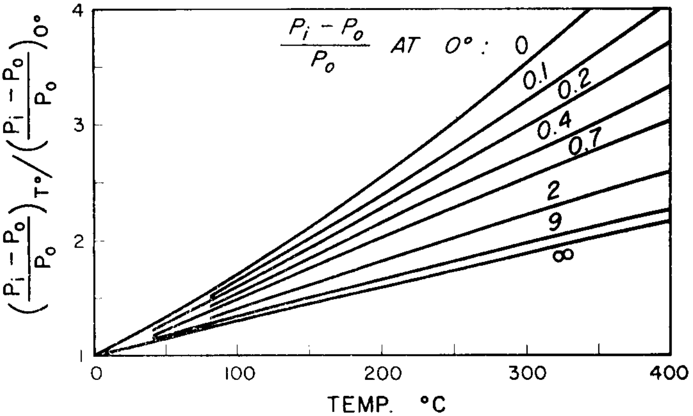

FIG. 1.—Change in relative pressure drop with temperature for columns with various pressure gradients (P_i is the inlet pressure, P_o is the outlet pressure and T is the temperature).

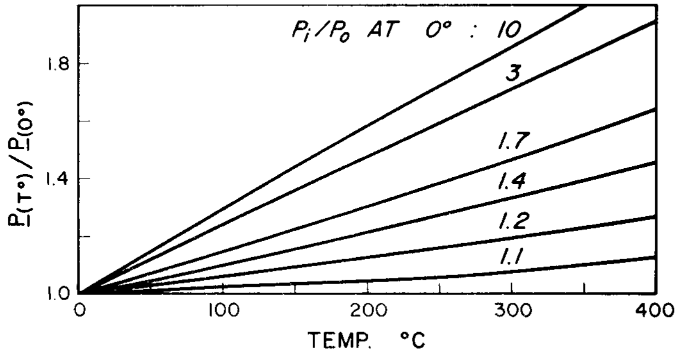

FIG. 2.—Change in inlet to outlet pressure ratio with temperature for columns with various pressure gradients.

If one assumes that the flow rate, expressed at column outlet pressure and at a constant temperature of 0°, is maintained constant (constant mass flow rate) while the temperature of the column is changed, then some pressure drop relationships which can be calculated are shown in Figs. 1 and 2. Fig. 1 indicates that the relative change in pressure drop with increased temperature is greatest when the absolute pressure drop across the column is smallest. It can be deduced that when the pressure drop is small, *i.e.*, $P_o - 1$ approaches zero, then the temperature dependence of $\underline{P} - 1$ varies according to $(T/273)^{1{\cdot}7}$, where $\underline{P}$ is the ratio of inlet to outlet pressure, P_i/P_o, and T is the column temperature. The power 1·7 arises from the 0·7 viscosity dependence and the 1·0 from thermal expansion. When the pressure drop is large $\underline{P} - 1$ varies according to $(T/273)^{0{\cdot}85}$. In Fig. 2 the actual changes in the ratio of inlet to outlet pressure with temperature are illustrated. As expected, this ratio changes most when it is high initially. The principal significance of these changes for the present work are in connection with the James and Martin[7] compressibility correction to flow-rates, *i.e.*, $j = \frac{3}{2}\frac{(P^2 - 1)}{(P^3 - 1)}$.

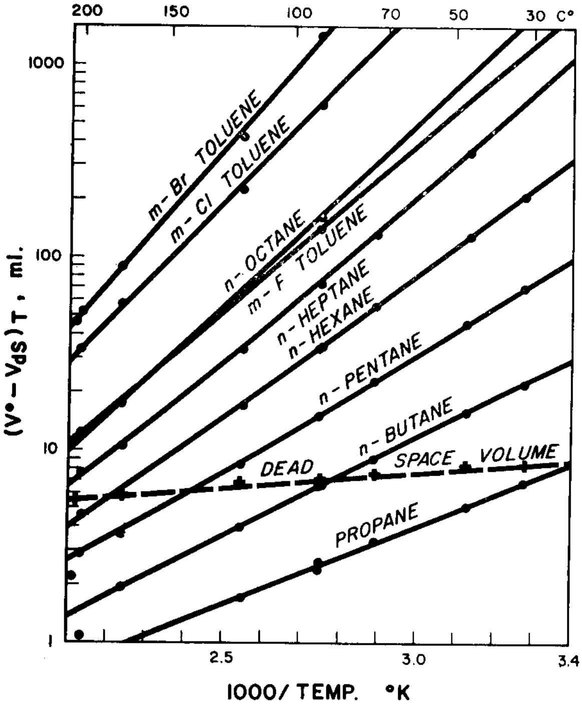

FIG. 3.—Dependence of net retention volume, ($V^\circ - V_{ds}$), per g of column liquid, on temperature for a variety of solutes on Apiezon L on firebrick (2-m, 0·25-inch coiled copper column).

Distribution coefficient

The most important effect of temperatures is on the distribution coefficients of the sample components between the eluent gas and the stationary liquid and is reflected primarily in the retention volumes and secondarily in the relative peak broadenings. The variation in distribution coefficient with temperature is dependent principally upon the exponential change of vapour pressure with temperature and to a small extent on changes in activity coefficients.[8] This leads to the well-known linear relationship between the logarithm of the net retention volume and the reciprocal of the absolute temperature, such as shown in Fig. 3.

Column efficiency

Column efficiency, or the number of theoretical plates, is commonly expressed in terms of the theoretical plate height, H, as a function of eluent gas velocity for any particular system at constant temperature. The spreading of a chromatographic band in a column has been shown to be caused by a number of factors. These may be summarised in the following expression involving eluent gas velocity

$$\mathrm{H} = \mathrm{A} + \mathrm{B/u} + \mathrm{C_{liq}\,uj} + \mathrm{C_{gas}\,u} \tag{1}$$

A, B, C_{liq} and C_{gas} are constants at any given temperature, u is defined here as the eluent gas velocity at the outlet, and j is the compressibility correction.

The first and controversial term A in equation (1) is the contribution from eddy diffusion. It is a term which is limited to packed columns and is ascribed to the multiple paths followed by the eluent gas. It is small and is considered negligible by some authors. If real, it should be independent of temperature and therefore need not concern us further.

The second term, B/u, which is most important at low flow velocities, describes the spreading because of diffusion in the flowing gas along the direction of flow. The constant B is $2\gamma D_g$, where D_g is the gas phase diffusion coefficient at column outlet conditions and γ is a tortuosity factor equal to somewhat less than 1 for a packed column. To assess the importance of this term it is necessary to know the diffusion coefficients and their change with temperature. The equation of Chen and Othmer[9] appears to agree with experimental measurements better than any other general equation yet proposed and the constants involved are the readily accessible critical constants:

$$\mathrm{D_{gas}} = \frac{0{\cdot}43\left(\dfrac{\mathrm{T}}{100}\right)^{1{\cdot}81}\left(\dfrac{1}{\mathrm{M_1}}+\dfrac{1}{\mathrm{M_2}}\right)^{0{\cdot}5}}{\mathrm{P}\left(\dfrac{\mathrm{T_{C_1}\,T_{C_2}}}{10{,}000}\right)^{0{\cdot}1405}\left[\left(\dfrac{\mathrm{V_{C_1}}}{100}\right)^{0{\cdot}4}+\left(\dfrac{\mathrm{V_{C_2}}}{100}\right)^{0{\cdot}4}\right]^{2}} \tag{2}$$

D_{gas} is the diffusion coefficient in cm^2/sec, T is the absolute temperature, P is the pressure in atmospheres, M_1 and M_2 are the molecular weights of eluent gas and diffusing solute, and T_{C_1}, T_{C_2}, V_{C_1} and V_{C_2} are the critical temperatures and volumes. This equation indicates that the diffusion coefficient is inversely proportional to pressure and, important for our present purposes, proportional to the 1·81-power of temperature. Thus, the gaseous diffusion coefficient increases strongly with temperature and, for instance, could be expected to double in going from 25° to 160°. For conditions of constant mass flow rate, the actual velocity at the column outlet is proportional to temperature to the first power. Hence, for constant mass flow rate conditions the B/u term increases with temperature according to only the 0·81-power.

The third and fourth terms in equation (1) refer to band broadening, which results from the finite time taken for equilibrium to be reached across any column section between the gas and liquid phases. The third term, $C_{\text{liq}}\ uj$, describes the effects of resistance to mass transfer in the liquid phase. The C_{liq} coefficient of this term is generally agreed to have the form

$$\mathrm{C_{liq}} = \frac{2}{3}\,\frac{\mathrm{k}}{(1+\mathrm{k})^2}\,\frac{\mathrm{d_{liq}^2}}{\mathrm{D_{liq}}} \tag{3}$$

where k is the ratio of moles of solute in the liquid to moles of solute in the gas, $\mathrm{d_{liq}}$ is the effective thickness of the liquid phase on the solid support and $\mathrm{D_{liq}}$ is the diffusion coefficient. In contrast to the second term, high diffusion coefficients minimise band broadening while high eluent gas velocities increase band broadening.

Experimental measurements of the diffusion coefficients of small solute molecules in high molecular weight viscous liquids are not very extensive, particularly over a range of temperatures. An estimate of the temperature dependence of diffusion coefficients may be made from viscosity measurements using the general relation that the diffusion coefficient is proportional to the absolute temperature divided by the viscosity. This quantity is plotted in Fig. 4 for a variety of solvents.[10] Variations over many orders of magnitude are clearly indicated. The temperature coefficient of viscosity, and hence of diffusion, appears to be particularly large for highly viscous liquids.

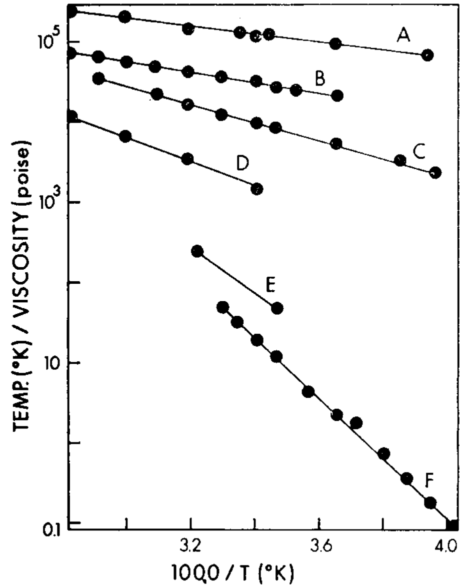

FIG. 4.—Viscosity-temperature relations for various substances:
A—ether, D—glycol,
B—carbon tetrachloride, E—heavy machine oil,
C—n-butyl alcohol, F—glycerol.

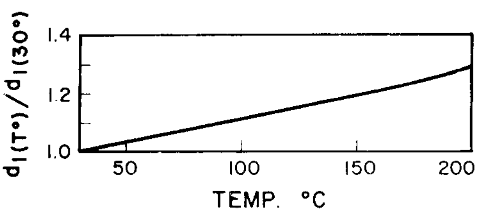

FIG. 5.—Relative thermal expansion of dinonylphthalate [$d_l(T°)$ is the effective thickness of liquid film at $T°$; $d_l(30°)$ is the effective thickness of film at 30°].

The absolute magnitude of the diffusion coefficient in liquids is very much smaller than in gases. Thus, Scott and Hazeldean[11] reported a value of 1·1 × 10^{-7} cm^2/sec for n-heptane in dinonylphthalate, which can be compared with a value of about 0·4 cm^2/sec for n-heptane in helium at a pressure of 1 atmos.

The remaining two factors contributing to C_{liq} [equation (3)] are also temperature dependent. The temperature dependence of the term d_{liq} is because of the thermal expansion of the liquid and Fig. 5 shows the relatively minor change in the relative value of d_{liq} as a function of temperature for dinonylphthalate.[12] Even though this factor is squared in equation (3) its temperature effect is still small.

Finally, the distribution ratio, k, as noted in the preceding section, varies exponentially with the reciprocal of the absolute temperature and hence will decrease strongly with increasing temperature. This is shown in Fig. 6 for three typical cases which are derived from the data of Fig. 3 and are chosen to represent cases of a substance with a very low retention volume, propane; one with an intermediate value, pentane; and one with a large retention volume, octane. The quantity $k/(1 + k)^2$ will have a maximum at k equal to 1 and thus starting from a high value of k at low temperature, $k/(1 + k)^2$ will first rise and then fall with temperature as shown in Fig. 7 for the same three examples. Normally k is somewhat greater than 1 for optimum chromatographic behaviour and, hence, the usual effect of increasing temperature will be to increase this factor.

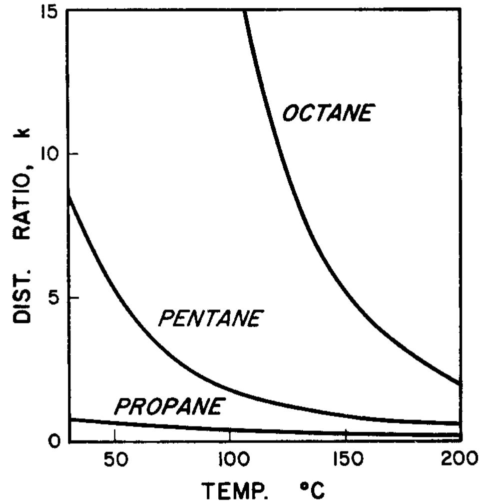

FIG. 6.—Distribution ratio, k, as a function of temperature for three hydrocarbons on an Apiezon L column using the data of Fig. 3.

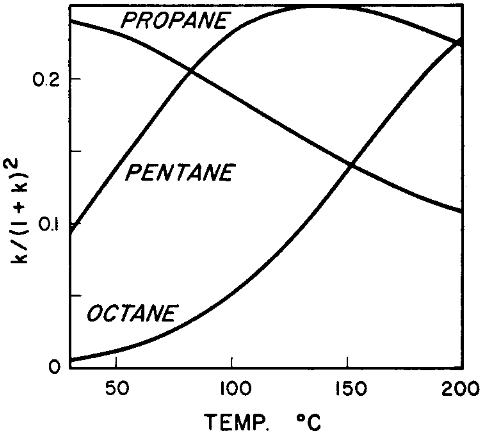

FIG. 7.—The factor $k/(1 + k)^2$ as a function of temperature for the three hydrocarbon systems.

When the temperature effects for all three factors of the third term are combined, the relative values of C_{liq} for the three hydrocarbon systems of Figs. 6 and 7 are obtained as functions of temperature (Fig. 8). In this figure it has been arbitrarily assumed that D_{liq} changes in the same way with temperature as does glycol, Fig. 4, and also that all three solutes have equal diffusivities. It can be seen that the highly volatile propane has a C_{liq} term decreasing strongly with temperature. For the more typical case of a strongly retained substance, such as octane, the factor is low and may even increase slightly with temperature. The contribution to plate height is equal to $C_{\mathrm{liq}}\, uj$. For operation at constant mass flow rate u increases in proportion to temperature, while j decreases to an extent dependent upon the initial pressure drop across the column as explained in the first section. The product uj will increase with temperature and this effect must be considered along with the data of Fig. 8. The joint and competing effects of these various factors results in a complex temperature behaviour for the third term of equation (1).

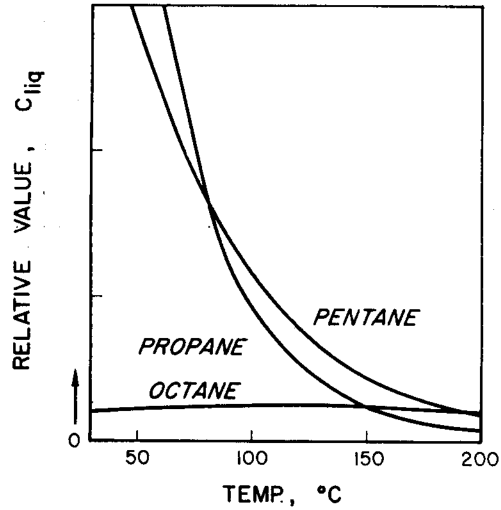

FIG. 8.—The relative value of the coefficient of resistance to mass transfer in the liquid phase, C_{liq}, as a function of temperautre.

Finally, the fourth term, $C_{\mathrm{gas}}\, u$, refers to band broadening from resistance to mass transfer in the gas phase, where C_{gas} is a constant expressed in terms of the outlet conditions of the column. This term is probably the least well understood except for capillary columns.[3,13] As a general expression, Jones[2] has proposed that

$$C_{\mathrm{gas}} = C_2 \frac{k^2}{(1+k)^2} \frac{d_{\mathrm{gas}}}{D_{\mathrm{gas}}} + C_3 \frac{d_p{}^2}{D_{\mathrm{gas}}} + 2\rho(C_2C_3)^{\frac{1}{2}} \frac{k}{(1+k)} \frac{d_p\, d_{\mathrm{gas}}}{D_{\mathrm{gas}}} \tag{4}$$

where C_2 and C_3 are constants, d_{gas} is the average diffusion path length in the gas phase, d_p is the packing particle size and ρ is a factor between 0 and 1. These three factors refer to diffusion in the gas phase, mixing of streams of gas with different velocities and to interactions between these two effects. On the other hand, Giddings[14] has suggested that the major effect arises from the interactions of relatively high velocity portions of the gas stream in the large interparticle spaces with the relatively stagnant or low velocity portions, such as in intraparticle pores. Qualitatively, all of these contributions to the plate height show a decrease with increasing temperature, primarily because of the D_{gas} factor which increases according to the 1·81-power of the temperature [equation (2)]. Factors involving k vary between 1 and 0, while d_{gas} would be expected to be essentially independent of temperature. To illustrate the magnitudes of the proposed effects Figs. 9, 10 and 11 show relative values of the three gaseous resistance terms proposed by Jones for the widely variant situations represented by propane, pentane and octane cited before. It can be seen that the first and third factors decrease sharply with temperature, whereas the second decreases more slowly. The relative change in a factor, such as the one proposed by Giddings,[14] would be nearly identical with the curves for Jones' second factor. The over-all contribution of the fourth term, $C_{gas}\,u$, includes the contribution of the gas velocity. At constant mass flow rate it must be borne in mind that u increases in direct proportion to the temperature.

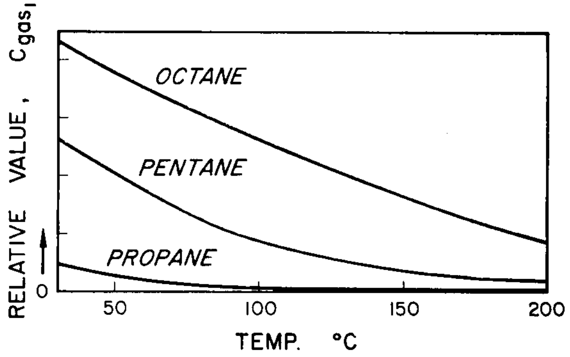

FIG. 9.—The relative value of C_{gas_1}, the first term in equation (4), as a function of temperature.

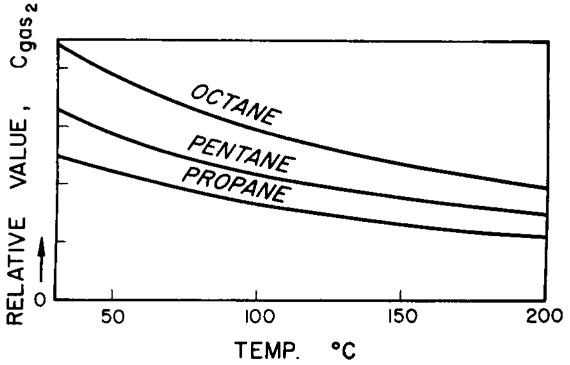

FIG. 10.—The relative value of C_{gas_2}, the second term in equation (4), as a function of temperature.

The contributions of the various terms of equation (1) to the final value of plate height for a particular column can vary independently over wide ranges. The data of the preceding figures and equations have been used to produce various sets of plate height—gas velocity curves (Fig. 12) for these same three hydrocarbon systems, propane, pentane and octane on Apiezon L, as representative of substances with low, intermediate and relatively high retention volumes. In order to combine the various terms of equation (1) the following conditions were specified:

1. The second term is 0·6 cm for propane at 30° and a value of u of 1 cm/sec. This is a reasonable value for a packed column at this low velocity.

2. The total contribution of the third and fourth terms is 0·1 cm for propane at the above conditions. This value for the mass transfer terms is arbitrary and would depend on the column packing.

3. The three contributions to C_{gas} in equation (4) apply in the ratio of 1:20:1. The proportions are arbitrary, but are influenced considerably by Giddings' conclusion.

4. Parts A, D and G of Fig. 12 are based on the term C_{liq} equal to the term C_{gas} for propane at 30°; parts B, E and H are based on C_{liq} equal to 10 C_{gas}; and parts C, F and J are based on C_{liq} equal to 100 C_{gas}, again for propane at 30°.

The results are further limited by the assumptions implied previously: helium carrier gas, outlet pressure of 1 atmos, negligible pressure drop, the term A equal to zero and a column liquid with the viscosity characteristics of glycol and the retention characteristics shown in Fig. 3. Following a usual convention the flow velocities shown are those measured at column temperature and at outlet pressure. If the velocity is expressed at some standard temperature in order to make comparisons under conditions of constant mass flow rate, then the figures are qualitatively similar but with the high temperature curves compressed towards the vertical axis.

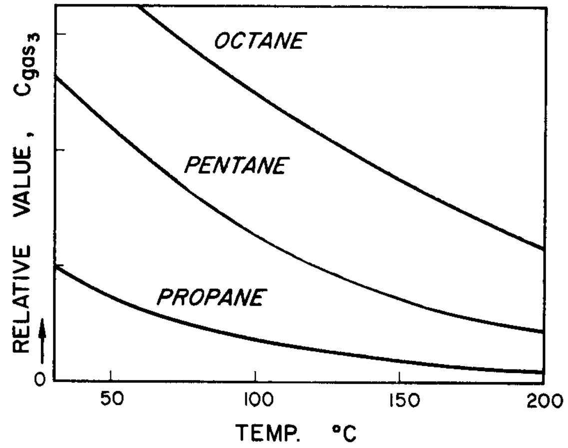

FIG. 11.—The relative value of C_{gas_3}, the third term in equation (4), as a function of temperature.

Fig. 12 illustrates most of the characteristics identifiable in experimentally observed curves. If one bears in mind that most chromatographic separations are based on k values in the range of 1 to 5, it can be seen from Fig. 6 that the three systems illustrated in Fig. 12 cover a much wider range of conditions than are usually employed in practice. Even at the lowest temperature of 30°, propane is still at the lower limit of useful retention while octane is only within this range in the upper 50° of the temperatures chosen.

At low velocities the predominant contribution to plate height arises from the term B, which decreases with decreasing temperature or increasing molecular weight of the sample component. The contribution of the term B becomes small at high velocities and for this reason will not be discussed in further detail.

At high velocities the mass transfer terms predominate. The general effect obvious from the various charts is a decrease in mass transfer resistance with increasing temperature although the curves in J are approaching the opposite behaviour.

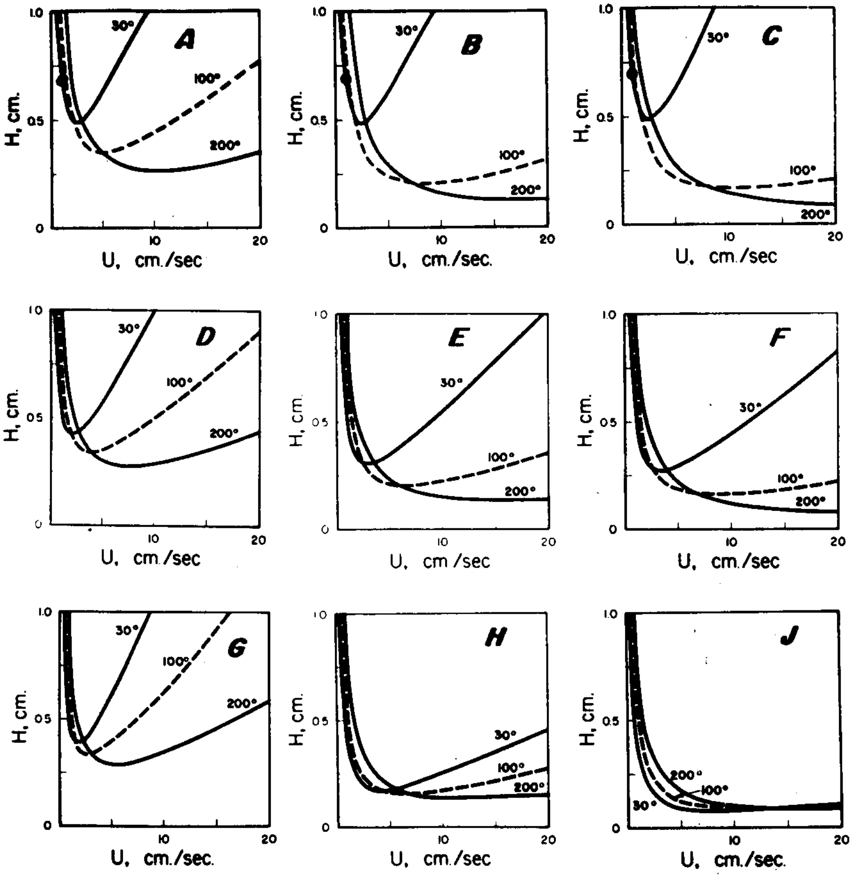

FIG. 12.—Calculated plate height—gas velocity curves for the same three systems of the previous figures at three temperatures and based on three arbitrary ratios of 1, 10 and 100 for C_{liq} to C_{gas} for propane at 30° [B/u of equation (1) taken as 0·6 cm and ($C_{liq}u + C_{gas}u$) taken as 0·1 cm for propane at 30° and u of 1 cm/sec]:

Temperature		30°		100°		200°	
Chart	Compound	C_{liq}	C_{gas}	C_{liq}	C_{gas}	C_{liq}	C_{gas}
A	propane	50	50	4·7	39	0·5	20
B	propane	91	9·1	8·6	7·1	0·8	3·7
C	propane	99	1·0	9·4	0·8	0·9	0·4
D	pentane	20	78	5·8	48	1·0	28
E	pentane	35	14	10	·87	1·8	5·1
F	pentane	38	1·6	12	0·9	2·0	0·5
G	octane	1·0	109	1·3	71	1·0	42
H	octane	1·9	20	2·4	13	1·8	7·6
J	octane	2·1	2·2	2·6	1·4	2·0	0·8

C_{liq} and C_{gas} given in sec × 10^3.

Charts A, D and G are based on equal contributions of the liquid- and gas-phase resistance to mass transfer for propane at 30°. The initial high temperature coefficient of C_{liq} for propane as well as the relative positions of the curves in Figs. 8 and 10 mean that the gas-phase contribution predominates at most temperatures and at all temperatures for the higher hydrocarbons. Thus, for instance, in A at 200° the contribution of liquid resistance to mass transfer is only about 2% of the gas-phase resistance. Charts A, D and G therefore illustrate the case of gas resistance being the major contribution to plate height. Under these conditions it is clearly advantageous to work at high temperatures. Furthermore, because of the relatively small effect of the distribution ratio on the value of C_{gas}, the curves for the different hydrocarbons are very similar to each other and high efficiencies may be attained at high temperatures for all components in an analysis. This type of operation is characteristic of most capillary columns which would therefore be expected to show a marked increase in efficiency with higher temperatures. This has been clearly demonstrated by Scott.[13]

At the other extreme in charts C, F and J, which are based on C_{liq} equal to 100 C_{gas} for propane at 30°, one sees curves in which liquid-phase resistance is generally predominant. At 200° both liquid and gas resistance to mass transfer are of the same order. Other generalisations are difficult because of the competing effects involved in the temperature coefficient of C_{liq}. With propane the decrease in $k/(1 + k)^2$ and of $1/D_{\text{liq}}$ with temperature combine to show marked increases in efficiency with increasing temperature in the range 30° to 100°. With pentane the large change in the factor $1/D_{\text{liq}}$ over-rides the increase in $k/(1 + k)^2$ in this same temperature interval and the curves are similar to those for propane. For octane the factors approximately compensate at all temperatures. Under these conditions the efficiencies may vary widely for the different components in a sample.

A case presumably similar to that in chart F has been described by Duffield and Rogers.[15] These authors have shown that liquid-phase viscosity affected plate height as would be expected for a column in which C_{liq} is controlling.

In a comparison of different ratios of liquid and gas resistances, such as shown in any horizontal row in Fig. 12, the effects to be expected will depend mostly on the type of temperature behaviour of the C_{liq} factor. Thus, for propane where C_{gas} and C_{liq} are qualitatively similar the temperature effects are not grossly different. For octane where the temperature coefficients of C_{gas} and C_{liq} are of the opposite sign over a wide temperature range, profound changes in the curves become evident in going from G to J.

It is not feasible to attempt to describe all of the possible extrapolations of the data shown in Fig. 12 to other possible conditions involving changes in gas and liquid properties. One case of possible interest would involve greater predominance of liquid-phase resistance, relatively high retention volume and possibly a lower temperature coefficient of liquid viscosity. A combination of these effects could lead to a marked decrease in column efficiency with increasing temperature, such as was almost reached in chart J. The curves shown in Fig. 13 may be an example of this sort. This figure shows the usual behaviour between 30° and 50°, but above 50° the efficiency appears to decrease with increasing temperature.

Further analysis of the relationships depicted in Fig. 12 may be made by considering the minimum plate height or maximum efficiency values and the corresponding velocities. The gas velocity at the minimum[16] in the plate height—velocity curves

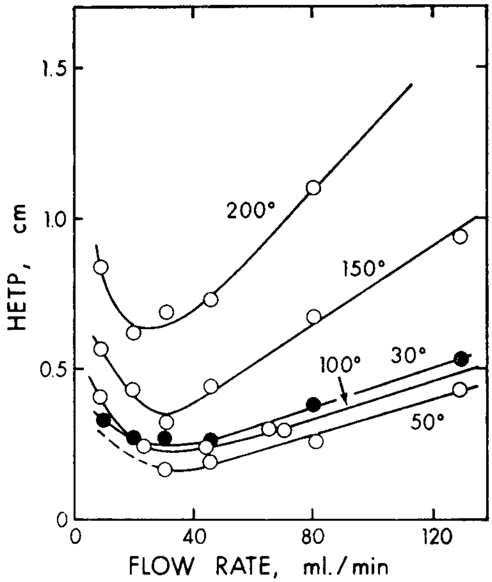

Fig. 13.—Plate height—gas velocity curves for n-hexane at a series of temperatures on a 2-M Apiezon L column using hydrogen as the carrier gas.

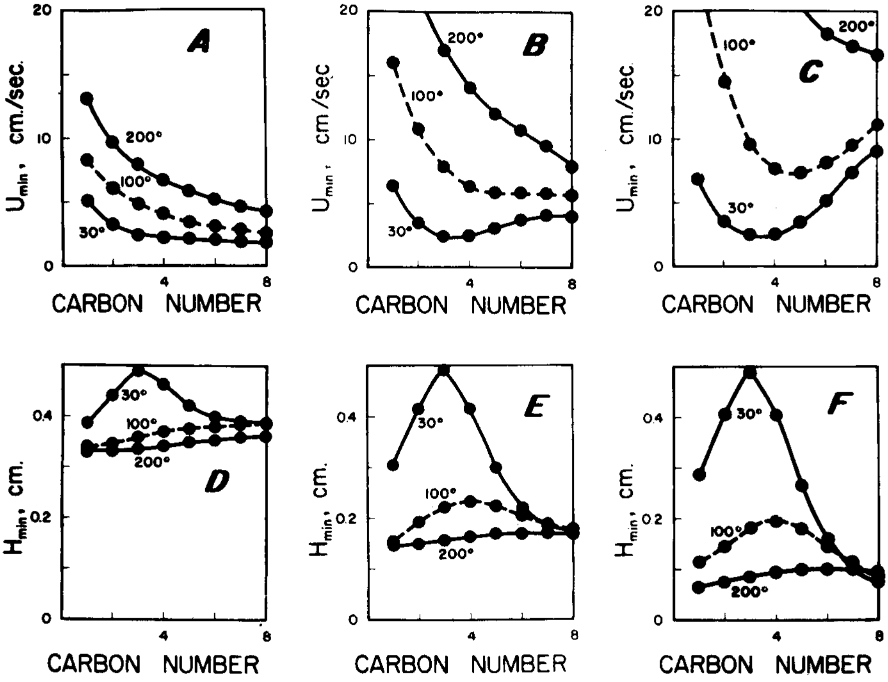

Fig. 14.—Optimum velocity and minimum plate height as a function of carbon number and temperature for hydrocarbons under conditions specified in Fig. 12:

A and D—Based on C_{liq} equal to C_{gas} for propane at 30°,
B and E—Based on C_{liq} equal to 10 C_{gas} for propane at 30°,
C and F—Based on C_{liq} equal to 100 C_{gas} for propane at 30°.

at any one temperature is equal to $\sqrt{B/(C_{liq} + C_{gas})}$ and the value of the plate height at this minimum velocity is equal to $A + 2\sqrt{B(C_{liq} + C_{gas})}$. In Fig. 14 these two quantities are shown as a function of carbon number at three column temperatures and for the three C_{liq}/C_{gas} conditions illustrated in Fig. 12. Reasonable estimates of the values of the retention characteristics of hydrocarbons not shown in Fig. 3 have been made. One may say generally that, for any one hydrocarbon, with increasing temperature the gas velocity at the minimum increases (charts A, B and C) and the H_{min} decreases (charts D, E and F). These effects are independent of the ratio of liquid- and gas-phase mass transfer resistances, although for octane in chart F a slight reverse trend in H_{min} is apparent. As indicated in the earlier discussion and possibly suggested in Fig. 13, this decrease in optimum efficiency with increasing temperature may occasionally be of some practical significance. At constant temperature the optimum velocity may decrease regularly with carbon number where gas phase resistances tend to predominate as in chart A; or it may show a more complex behaviour when liquid phase resistances become significant as in charts B and C. The H_{min} values are relatively independent of carbon number at higher temperatures but vary considerably through a maximum at lower temperatures. The variations in both U_{min} and H_{min} are greatest when liquid-phase resistances predominate.

It is obvious from Figs. 12 and 14 that flow conditions cannot be chosen at any one temperature which will result in maximum efficiencies for all solutes. This is recognised in chromatographic practice in that a gas velocity greater than the minimum is usually chosen.

It should be emphasised that while the conditions assumed for the construction of the curves in Figs. 12 and 14 may exemplify actual chromatographic conditions there are innumerable alternatives. For example, the mass transfer terms may be larger or smaller compared to the longitudinal diffusion term, the gaseous mass transfer term may be more or less important, *etc.* Normally, one attempts by appropriate selection of design and operating variables to minimise both mass transfer contributions to plate height. Thus, changing the carrier gas to one with low diffusivity will decrease the longitudinal diffusion term but increase the term C_{gas} and leave the term C_{liq} unchanged. The relative values of C_{gas} and C_{liq} will also depend on column or particle dimensions and on the manner in which the liquid is distributed on the support. The effects of various combinations can be deduced from reasonable extensions of the data given by the curves shown in Fig. 12. For example, a ten-fold decrease of the terms C_{liq} and C_{gas} of A, D and G would produce three new figures all very similar to H.

Zusammenfassung—Der zu erwartende Temperatureinfluß auf die Wirksamkeit von Säulen wird im einzelnen für typische Verbindungen niedriger, mittlerer und hoher Retention erörtert. Es werden Fälle mit verschieden großer Hemmung des Massenüberganges in Gas- und flüssiger Phase betrachtet. Es wird gefolgert, daß bei einer Temperatur keine für alle gelösten Stoffe optimal wirksamen Strömungsbedingungen zu finden sind. Es ist auch zu erwarten, daß die Wirksamkeit der Säule im allgemeinen mit steigender Temperatur zunehmen sollte, obwohl unter gewissen Bedingungen, nämlich starker Hemmung des Massenüberganges in der flüssigen Phase relativ zur Gasphase, ein Abfall oder scheinbare Unabhängigkeit von der Temperaturge funden werden kann. Außerdem wird kurz der Einfluß der Säulentemperatur auf den Druckabfall längs der Säule untersucht.

Résumé—On étudie en détail les effets de la température sur l'efficacité d'une colonne dans le cas de composés caractéristiques de haute, moyenne et basse rétention. On analyse des exemples comportant diverses valeurs relatives de la résistance au transfert de masse tant en phase liquide qu'en phase vapeur. On montre qu'on ne peut trouver des conditions de reflux à une température donnée, telles qu'on puisse obtenir l'efficacité maximale pour tous les solutés. On montre également que l'efficacité de colonne croit généralement avec la température. Cependant, dans certaines conditions, si le rapport des résistances au transfert de masse en phase liquide et en phase gazeuse est grand, on peut rencontrer une décroissance ou une pseudo-indépendance par rapport à la température. On examine également brièvement la variation de la température de la colonne sur la chute de pression le long de la colonne.

REFERENCES

[1] J. J. Van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, 1956, **5**, 271.
[2] W. L. Jones, *Analyt. Chem.*, 1961, **33**, 829.
[3] J. C. Giddings, *ibid.*, 1963, **35**, 439.
[4] M. J. E. Golay in *Gas Chromatography* 1958, D. H. Desty, ed. Academic Press, New York, 1958, p. 36.
[5] H. W. Habgood and W. E. Harris, *Analyt. Chem.*, 1960, **32**, 450.
[6] O. A. Hougen and K. M. Watson, *Chemical Process Principles*, Part three, *Kinetics and Catalysis.* Wiley, New York, 1947, p. 871.
[7] A. T. James and A. J. P. Martin, *Biochem. J.*, 1952, **50**, 679.
[8] A. B. Littlewood, *Gas Chromatography.* Academic Press, New York, 1962, p. 78.
[9] N. H. Chen and D. F. Othmer, *J. Chem. Eng. Data*, 1962, **7**, 37.
[10] *Handbook of Chemistry and Physics.* Chemical Rubber Pub. Co., Cleveland, U.S.A., 43rd Edition.
[11] R. P. W. Scott and G. S. Hazeldean in *Gas Chromatography,* R. P. W. Scott, ed. Butterworth, London, 1960, p. 144.
[12] E. R. Adlard, M. A. Khan and B. T. Whitham, *ibid.*, p. 253, reference 11.
[13] R. P. W. Scott, *J. Inst. Petroleum*, 1961, **47**, 452.
[14] J. C. Giddings, *Analyt. Chem.*, 1962, **34**, 1186.
[15] J. J. Duffield and L. B. Rogers, *ibid.*, 1960, **32**, 341.
[16] J. H. Purnell, *Gas Chromatography.* Wiley, New York, 1962, p. 189.

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THERMOMETRIC TITRATIONS IN ACETONITRILE

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Summary—The use of acetonitrile as a medium for thermometric acid-base titrations has been studied. Satisfactory titrations are obtainable for a wide variety of amines and organic acids, but the instability of the solvent in the presence of strong bases greatly limits its practical applicability. Data are given on the heats of neutralisation of various acids in acetonitrile, and the results for *m*- and *p*-substituted benzoic acids are shown to correlate well with their Hammett σ-values.

INTRODUCTION

THE advantages of performing acid-base titrations in non-aqueous systems are well known. The limitations of conventional methods of end-point detection have led to the exploration of alternatives. One of these, automatic thermometric titrations, introduced by Linde, Rogers and Hume,[1] is particularly well adapted to non-aqueous systems because of its independence of the chemical nature of the solvent and reactant. A general review has been given by Zenchelsky.[2] The applicability of thermometric titration to non-aqueous acid-base titrations in glacial acetic acid has been studied by Keily and Hume.[3] The present paper describes the investigation of acid-base titrations in acetonitrile.

Acetonitrile is a good solvent for a wide variety of organic acids and bases. Being very weakly basic and having negligible acidic properties, it permits titrations to be made over a very wide range of acidity as compared to water. Fritz,[4] carrying out potentiometric titrations with a glass-calomel electrode pair, showed that acetonitrile was a suitable solvent for differentiating titrations of strong and weak bases. Critchfield and Johnson[5] demonstrated acetonitrile to be a satisfactory solvent for differentiating potentiometric titrations of relatively strong acids. This lack of leveling action also shows in its range between the half-neutralisation potentials of strong acids and strong bases which Van der Heijde and Dahmen[6] observed to be one of the widest among the solvents which have been studied, being better in this respect than acetic acid, dimethylformamide, ethanol or amines. In practice, however, the range is limited somewhat by the effect of very strong bases, such as hydroxide ion or alkoxide, which catalyse the polymerisation of solvent.

EXPERIMENTAL

Apparatus

The instrumental set-up used was that designed, built and employed by Keily.[7] A constant-flow, motor-driven syringe burette delivers titrant into the sample, which is contained in a half-pint Dewar flask. The flask carries a Plexiglass cover insulated with cork, which holds the measuring thermistor, a glass-covered wire heater, and has holes for the burette tip and the shaft of a 600-rpm stirrer. The temperature of the titration mixture is measured continuously by a thermistor in a Wheatstone bridge circuit and recorded on a Speedomax G, 2-mV potentiometer-recorder. Pen displacement has been shown to be linear with temperature changes over a range of several tenths of a degree, and the instrument at the highest sensitivity responds to a change of 0·001°. Titrations were performed by first adjusting the temperature of the sample to that of the titrant, then running in the titrant at constant speed with a continual recording of the temperature.

Reagents

Acetonitrile: Material obtained from Carbide and Carbon Chemicals Co. was used throughout this work. The water content of the material as received was of the order of 0·1% (by Karl Fischer titration) and, occasionally, small amounts of weakly acid impurities appeared in individual batches. The presence of acidic impurity was tested for by the addition of 1 drop of thymol blue (salt form) to about 5 ml of solvent. In satisfactory material the colour should be yellow (red indicates acidic impurity) and should change to blue upon the addition of not more than 1 drop of 0·1*M* sodium methoxide in methanol.[7] Water and other impurities were removed in either of two ways. One method consisted of predrying with anhydrous potassium carbonate, then distilling over phosphorus pentoxide. This gave an excellent product at the expense of considerable time and effort. Another method which was employed throughout the bulk of this work involved drying the solvent by placing it in contact with Type 4A molecular sieves (Linde Air Products Co.) for at least 15 min before use. The solvent treated in this way was found to contain less than 0·01% of water and the absorbant properties of these sieves were sufficient to remove small amounts of acid impurities.

Substances titrated: Most of the bases titrated were subjected to some preliminary treatment or purification. They were of the best grades readily available, and all were Eastman White Label products unless otherwise noted. Compounds used without further purification were *p*-toluidine, *p*-bromaniline, *m*-nitro-aniline, ethylamine (anhydrous), trimethylamine (anhydrous), isopropylamine and urea (Merck U.S.P.).

Compounds distilled under vacuum were *o*-chloraniline, *N,N*-dimethylaniline, *N,N*-diethylaniline, *N*-methylaniline, aniline (Fisher Reagent), *p*-chloraniline (Eastman Practical), tri-n-butylamine (over sodium hydroxide) and tri-isobutylamine (Kahlbaum over sodium hydroxide).

Compounds subjected to simple distillation were isobutylamine (over calcium oxide), tert-butylamine (over calcium oxide), n-butylamine (over calcium oxide), 1-ethylpiperidine, pyridine (Mallinckrodt Reagent over sodium hydroxide), morpholine (Carbide and Carbon Co. over sodium hydroxide), n-propylamine (over sodium hydroxide), di-n-butylamine (over sodium hydroxide), diethylamine (Sharples Commercial over sodium hydroxide), triethylamine (Sharples Commercial over sodium hydroxide), sec-butylamine (Sharples over sodium hydroxide), di-sec-butylamine (Sharples over sodium hydroxide), and di-isopropylamine (Eastman Yellow Label over sodium hydroxide).

Ammonia (Matheson Co., Anhydrous) was passed through No. 4A Molecular Sieves (Linde Air Products Co.), then dissolved by passing it over a stirred volume of acetonitrile. The *p*-nitroaniline and *p*-chloraniline were recrystallised from ethanol and air-dried, while *p*-anisidine was recrystallised once from water and once from 10% methanol-water solution and finally washed with iced water and air-dried.

Compounds titrated as acids were prepared or purified in the following ways. No further purification was given to benzoic acid, *p*-toluic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-chlorobenzoic acid, *m*-chlorobenzoic acid, *m*-bromobenzoic acid, glacial acetic acid (duPont 99·7%), formic acid (Baker and Adamson 98–100%) or sulphuric acid (duPont 98%).

Monochloracetic acid was dried over phosphorus pentoxide for 24 hr, then vacuum-sublimed at about 60°. Dichloracetic acid (Eastman technical grade) was vacuum-distilled and trichloracetic acid (Mallinckrodt Reagent) was dried for 1 week over magnesium perchlorate and vacuum-sublimed at about 60°. The water content of the compounds before solution in acetonitrile was determined by Karl Fischer titration and found to be 0·25%, 0·12% and 0·09% for the mono-, di- and trichloracetic acid, respectively.

Titrants: Hydrogen bromide solutions in acetonitrile were used for the titration of organic bases. The titrant was usually made up to a concentration of approximately 0·1*M*. Solutions were prepared by passing anhydrous hydrogen bromide (Matheson Co.) through a drying tower containing anhydrous magnesium perchlorate and silica gel and then over the surface of the acetonitrile, which was being stirred vigorously with a magnetic stirrer. The resulting solutions generally developed a yellow colour in a period of 1–2 hr, but appeared to be stable thereafter. A similar colour developed when anhydrous solutions of hydrogen chloride were prepared, or when attempts were made to prepare anhydrous solutions of perchloric acid in acetonitrile. Hydrogen bromide appears to have a considerable vapour pressure over acetonitrile solutions: standard solutions were observed to decrease in strength by about 1% per day. For this reason the titrants were standardised daily by diluting aliquots with water and titrating with standard sodium hydroxide using a potentiometric end-point.

Diphenylguanidine solutions were used to titrate acids. Eastman White Label 1,3-diphenylguanidine was recrystallised successively from toluene, ethanol and again from toluene before being dried at 110° over-night. The resulting product was found to be $99{\cdot}7^{+}$% pure by titration with standard aqueous hydrochloric acid. Titrant solutions made with this product were colour-stable and did not change titre appreciably over a period of at least 1 month.

Procedure

The bases listed previously were all titrated with approximately 0·1*M* hydrogen bromide in acetonitrile. The solutions titrated were made up to about ten-fold more dilute than the titrant. In each instance, 15-ml portions were titrated. No corrections were made for density variations because all titrations were performed in an air-conditioned room with temperature fluctuations $\ngtr \pm 1^\circ$. In order to estimate the accuracy of the method, comparison was made between concentrations determined thermometrically and those determined by conventional methods. The concentration of aliphatic amines was determined by diluting aliquots about five-fold in water and titrating with standard aqueous hydrochloric acid, using either a glass-calomel potentiometric end-point or a methyl red–methylene blue mixed indicator. Aromatic amine concentrations were determined by dissolving aliquots in glacial acetic acid and titrating with perchloric acid in glacial acetic acid. The perchloric acid was standardised against potassium hydrogen phthalate using a glass-calomel electrode pair for potentiometric end-point determination.

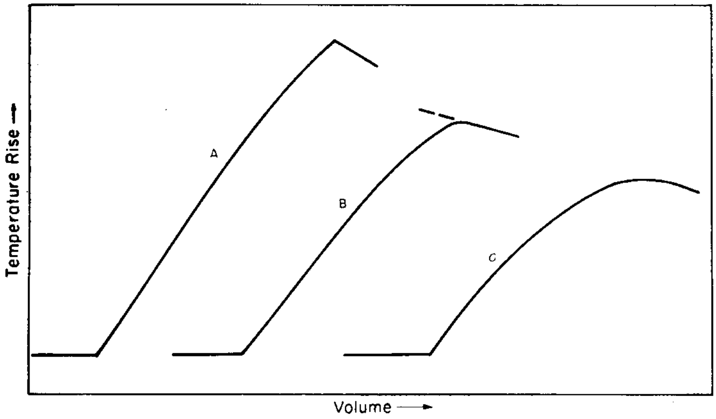

FIG. 1.—Typical titration curves of bases with a strong acid in anhydrous acetonitrile medium:
(A) aliphatic amines, (B) aromatic amines, (C) very weak bases.

RESULTS

Thermometric titration end-points consist of a change in slope of a temperature *vs.* volume curve. Typical curve shapes for the systems studied in this investigation are illustrated in Fig. 1. The ease of end-point estimation is evidently dependent upon the sharpness of the slope change. This, in turn, is related to two fundamental factors: the magnitude of the free-energy change of the reaction and the change in enthalpy which accompanies the reaction. Because it is the free-energy change which determines whether and how far a reaction will go towards completion, the magnitude of this term is of fundamental importance. Assuming a favourable free-energy change, the sharpness of the end-point break will be determined by the magnitude of the enthalpy change: the larger the change, the more acute the change in slope at the equivalence point. If the free-energy change in not favourable, there will be a rounded end-point because of the incompleteness of the reaction at the equivalence point, regardless of the magnitude of the enthalpy term. Because the temperature rise in thermometric titrations is nearly linear, rounded end-points may be estimated by extrapolation of the slopes before and after the highly curved portion of the plot. The general theory of the shape and characteristics of thermometric titration curves has been discussed by Keily and Hume.[9]

Titration of bases

Fig. 1 illustrates the general shapes of titration curves obtained for the titration of strong, weak and very weak bases with hydrogen bromide solution. It demonstrates the rough rule that sharpness of the end-point depends on the strength of the base titrated. This generalisation held in a qualitative sense for all of the bases titrated in this study. It is evident, however, from the data of Table I showing the precision and accuracy obtained in the titration of 17 non-aromatic amines that sharpness of the end-point is not the only factor which affects the precision and accuracy. The bases in Table I are listed in the general order of decreasing strength as determined by ionisation constant in water. It was noted that the precision for a number of the more volatile compounds was lower than that for the average, and this is probably a factor which contributes to the considerable range in standard deviations observed. The over-all percentage standard deviation from the pooled data of all of the titrations of bases is ±0·52%. This precision is poorer than the ±0·2% reported by Linde, Rogers and Hume for thermometric titrations in water[1] and by Keily and Hume for glacial acetic acid.[3] The observed precisions are similar to those reported by Fritz for potentiometric titrations.[4] It is of interest to note that the precision of titration of very weak bases was not significantly different from that of the over-all precision, even though the accuracy was lower. Table II shows results for aromatic and heterocyclic amines. With the exception of the values for *p*-bromaniline and *m*-chloraniline, the average accuracy is 99·2%. The latter compound defined the limits of practical titrability using the thermometric end-point in acetonitrile. All weaker bases, as measured by their pK_B values in water, gave thermometric curves which were so rounded that no significant change in slope could be seen to define the end-point. The weakest bases with discernible end-points have aqueous pK_B values in the range of 10–10·5. As is evident in the accuracy values for *p*-brom- and *m*-chloraniline, the tendency is for the observed end-point to err on the high side in the titration of very weak bases. A similar tendency is apparent in Keily's data for the titrations of the very weak bases, urea and acetanilide, in glacial acetic acid.[3]

TABLE I.—TITRATION OF NON-AROMATIC AMINES

Compound	No. of detns.	Present, *mmole*	Found *mmole*	Accuracy, %	Std. devn., %
Di-n-butylamine	4	0·600	0·598	99·7	0·14
Diethylamine	3	0·595	0·598	100·5	0·40
Di-sec-butylamine	4	0·285	0·281	98·6	0·76
Di-isopropylamine	3	0·130	0·129	99·2	1·56
Tri-n-butylamine	4	0·598	0·595	99·5	0·56
Ethylamine	3	0·535	0·529	98·9	0·93
Triethylamine	4	0·439	0·436	99·3	1·10
Isopropylamine	2	0·700	0·693	99·0	1·64
n-Butylamine	4	0·540	0·537	99·4	1·0
n-Propylamine	4	0·445	0·440	98·9	0·40
Sec-butylamine	2	0·535	0·531	99·3	0·0
Tert-butylamine	4	0·449	0·446	99·3	0·35
Iso-butylamine	3	0·995	0·983	98·3	0·70
1-Ethylpiperidine	4	0·111	0·110	99·1	0·97
Tri-isobutylamine	4	0·365	0·361	98·9	0·26
1,3-Diphenylguanidine	4	0·7079	0·7057	99·7	0·57
Ammonia	4	1·320	1·316	99·7	0·95

TABLE II.—TITRATION OF AROMATIC AMINES AND OTHER WEAK BASES

Compound	No. of detns.	Present, *mmole*	Found, *mmole*	Accuracy, %	Std. devn., %
Morpholine	4	0·424	0·420	99·1	0·85
N,*N*-Diethylaniline	4	0·457	0·449	99·1	1·03
p-Anisidine	3	0·640	0·634	99·1	0·40
Pyridine	4	0·590	0·584	99·0	0·74
p-Toluidine	4	0·828	0·824	99·5	0·23
N,*N*-Dimethylaniline	3	0·610	0·604	99·0	0·94
N-Methylaniline	3	0·640	0·628	98·1	1·14
Aniline	4	0·930	0·918	98·7	0·78
p-Chloraniline	4	1·028	1·033	100·5	1·23
p-Bromaniline	4	0·794	0·823	103·6	0·21
m-Chloraniline	4	0·820	0·853	104	1·12
o-Chloraniline	5		too weak to titrate		
m-Nitroaniline	3		too weak to titrate		
p-Nitroaniline	6		too weak to titrate		
Urea	4		too weak to titrate		

The effect of precipitation of insoluble hydrobromides during the titration is seen in Fig. 2. The sudden appearance of the heat of precipitation distorts the curve but need not affect the accuracy of locating the end-point if the onset of precipitation is not too close to the end-point. The heat of neutralisation may, of course, be estimated independently of the precipitation by the use of the initial slope.

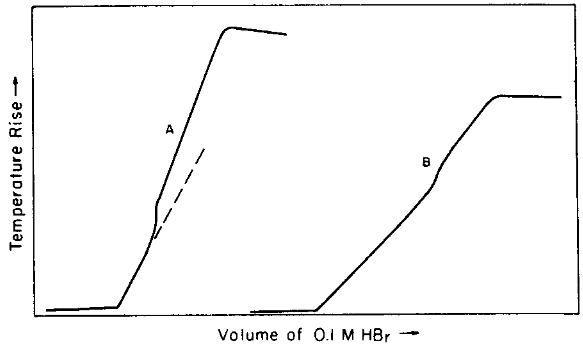

FIG. 2.—The effect of delayed precipitation during titration:
(A) aniline with hydrogen bromide,
(B) *p*-toluidine with hydrogen bromide.

Differentiating titration of bases

The criteria for a good differentiating end-point are evident from a consideration of the factors affecting the thermometric end-point in general. For successful thermometric differentiation, not only must the free-energy change for each component in the mixture be great enough to assure completeness of reaction, and the free energies be sufficiently different that the reactions take place consecutively, rather than simultaneously, but the enthalpy change for each component must be sufficiently different that a significant change in slope can be recognised. It is difficult to say exactly how much of a difference in ΔH is essential to end-point discernment because in real titrations extraneous factors, such as heats of dilution, heat loss and changing heat capacity from addition of titrant, also act to obscure end-points. It appears that roughly a slope ratio of the order of 3:2 for the components is necessary in order that the break be clearly defined. It has been shown that in acetonitrile there is a remarkably constant proportionality between ΔH and pK_B for amines of similar type.[10] Because the slopes of thermometric titration curves are proportional to ΔH, this means that two bases which are sufficiently different in strength to be titrated consecutively are likely to have thermometric slope ratios favourable for differentiating titration in acetonitrile. As an illustration of the types of curves obtained, Fig. 3 shows the titration of mixtures of 1,3-diphenylguanidine (ΔH = 20·7 Kcal/mole) plus pyridine (ΔH = 14·4 Kcal/mole), and mixtures of *N*-butylamine (ΔH = 25·8 Kcal/mol) plus pyridine. The titration of the diphenylguanidine-pyridine mixture is illustrative of borderline conditions of titrability. The precisions of the two end-points (standard deviation) are 1·14 and 1·16%, respectively. The titration curve for butylamine and pyridine is an example of an easily differentiated mixture. Precisions of these end-points are 0·5% and 0·61%, respectively.

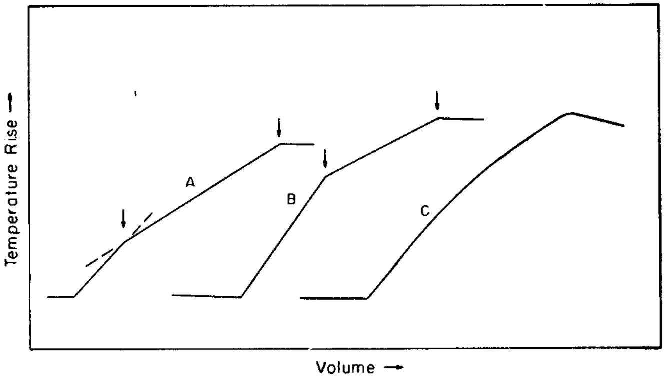

FIG. 3.—Differentiating titrations:
(A) 1,3-diphenylguanidine and pyridine with hydrogen bromide,
(B) *n*-butylamine and pyridine with hydrogen bromide,
(C) Sulfuric acid with 1,3-diphenylguanidine.

Titration of acids

The list of acids titrated with diphenylguanidine solution is given in Table III. The weakest acid that showed a distinct end-point was benzoic (pK_a in water 4·20). Acetic acid and *p*-toluic acids were too weak to be estimated thermometrically, in agreement with Kilpatrick,[8] who found that acetic acid could not be titrated in acetonitrile using indicators. The reason for the limitation to relatively strong acids is related to the instability of the solvent in the presence of strong bases. Presumably, if one could titrate with bases stronger than diphenylguanidine or aliphatic amines, the range of titrability could be greatly extended. This is indicated by the work of Bruss and Wyld,[11] who claimed that acids as weak as the phenols could be titrated in acetonitrile if tetrabutylammonium hydroxide in isopropyl alcohol was used as titrant. Attempts to dissolve bases such as potassium hydroxide or sodium methoxide in acetonitrile resulted in the formation of a reddish-brown gelatinous residue, presumably polymeric in nature. The over-all pooled percentage standard deviation for the titration of acids was found to be 0·99%.

TABLE III.—TITRATION OF ACIDS WITH 1,3-DIPHENYLGUANIDINE

Acid	No. of detns.	Present, *mmole*	Found, *mmole*	Accuracy, %	Std. Devn., %
Benzoic	3	0·302	0·309	102·3	1·21
p-Chlorobenzoic	3	0·269	0·275	102·3	2·4
m-Chlorobenzoic	3	0·0910	0·0903	99·2	1·55
m-Bromobenzoic	3	0·240	0·243	101·3	1·35
m-Nitrobenzoic	3	0·449	0·445	99·1	1·05
p-Nitrobenzoic	3	0·296	0·300	101·4	2·18
p-Toluic	6		too weak for end-point estimation		
Acetic	4		too weak for end-point estimation		
Chloracetic	2	0·470	0·476	101·3	1·58
Dichloracetic	3	0·313	0·311	99·4	0·60
Trichloracetic	3	0·114	0·113	99·1	2·08
Hydrogen chloride	3	0·606	0·603	99·5	0·47
Hydrogen bromide	4	0·428	0·424	99·1	0·77
Sulphuric[a]	3	0·426	0·424	99·5	0·33
Perchloric[b]	3	0·350	0·348	99·4	0·13
				pooled = ±0·99%	

[a] Both protons.
[b] Filtrate from barium perchlorate plus sulphuric acid reaction.

The titration of sulphuric acid with 1,3-diphenylguanidine is also shown in Fig. 3. Critchfield and Johnson showed that the two protons of sulphuric acid can be distinguished potentiometrically by titration with morpholine in acetonitrile solution. In the present instance, the free energy criterion appears to be fulfilled, but the difference in the heats of neutralisation of the two protons is not sufficiently great to allow a distinct evaluation of the first end-point.

Effect of water

Unfavourable effects from the presence of water in non-aqueous titration systems have been noticed by many authors. For the most part, interference from water is associated either with its acid-base properties or its high dielectric constant. Keily and Hume have also pointed out the problems from the heats of dilution and mixing that may result from the presence of even minute amounts of water.[3]

The situation is even more complex in acetonitrile where the possibility of acid- or base-catalysed hydrolysis of the solvent must also be considered. In the titration of solutions of hydrogen chloride with diphenylguanidine, there is little effect from the presence of 1–2% of water added immediately before the titration. If, however, as short a time as 1 hr elapses between the addition of water to the acid solution and the titration, as little as 0·5% of water can result in sufficient hydrolysis of the solvent to obscure the entire titration curve. On the other hand, there appears to be little perceptible effect of water on the titration of bases with hydrogen bromide.

In contrast with the behaviour of dry acetic acid systems, the presence of small amounts of water was found to have very little effect on the heat of dilution of the titrants. On running 0·1M hydrogen bromide into 50-ml portions of acetonitrile containing varying amounts of water, linear dilution curves of low slope were obtained. Even with 1% of water present, the temperature rise did not exceed 0·08°. Mixing studies with diphenylguanidine titrant and acetonitrile-water mixtures yielded similar results.

TABLE IV.—HEATS OF REACTION OF ACIDS WITH 1,3-DIPHENYLGUANIDINE

Acid	No. of detns.	$-\Delta H_{180}$, *Kcal/mole*	Std. devn., *Kcal/mole*	$pK_{A(H_2O)}$
Benzoic	3	12·4	0·2	4·20
p-Chlorobenzoic	4	12·8	0·8	3·98
m-Chlorobenzoic	4	12·8	0·3	3·82
m-Bromobenzoic	3	12·8	0·1	3·81
m-Nitrobenzoic	5	15·4	0·6	3·49
p-Nitrobenzoic	7	13·4	0·4	3·42
Chloracetic	5	13·6	0·9	2·86
Dichloracetic	3	15·7	0·5	1·30
Trichloracetic	3	19·2	0·6	0·89
Hydrogen bromide	3	20·3	0·2	—
Hydrogen chloride	7	25·3	0·7	—
Sulphuric[a]	6	20·4	1·4	—
Perchloric[b]	4	17·4	0·8	—
Perchloric[c]	4	17·6	0·5	—

[a] First proton.
[b] Filtrate from barium perchlorate plus sulphuric acid reaction.
[c] Contains excess glacial acetic acid.

DISCUSSION

Although satisfactory titrations may be obtained both for the titration of acids and of bases, the use of acetonitrile as a medium for acid-base titration with a thermometric end-point has no real advantage from a practical standpoint. The instability of the solvent in the presence of strong bases makes the determination of weak acids impractical, and the difficulty of preparing stable anhydrous acetonitrile solutions of strong acids is a drawback for the determination of bases. Attempts to prepare anhydrous acetonitrile solutions of perchloric acid by metathetical reactions were unsuccessful. For example, although barium sulphate is very insoluble in acetonitrile, a mixture of barium perchlorate and sulphuric acid continued to deposit a precipitate after equilibration for 6 months. Hydrogen bromide, in spite of its volatility, was the most satisfactory of the strong acids investigated. The utilisation of reagent solutions in solvents other than acetonitrile (*e.g.*, higher alcohols, ketones, dioxan) for titrations in an acetonitrile medium may generally be expected to give rise to heats of mixing and dilution which distort the titration curves and may not always be compensatable by differential temperature measurements.

The heats of reaction of carboxylic and mineral acids in acetonitrile with 1,3-diphenylguanidine are given in Table IV. It was of interest to see if the same sort of relationship existed between the heats of neutralisation of the carboxylic acids in acetonitrile and their acid strengths as was found to exist between the heats of neutralisation and basic strengths of amines in the same solvent.[10] The plot of $-\Delta H_{180}$ in acetonitrile *versus* the Hammet σ-value for benzoic acid and five *m*- or *p*-substituted benzoic acids (Fig. 4) shows that such a correlation does exist except for *m*-nitrobenzoic acid. The anomalously high value for the heat of neutralisation of this compound remains unexplained. The equation of the line in Fig. 4 is $-\Delta H_{180} = 1{\cdot}23\ \sigma + 12{\cdot}4 \pm 0{\cdot}1$ Kcal/mole. Data on the heats of neutralisation of 32 amines with hydrogen bromide in acetonitrile and their theoretical interpretation have been published elsewhere.[10]

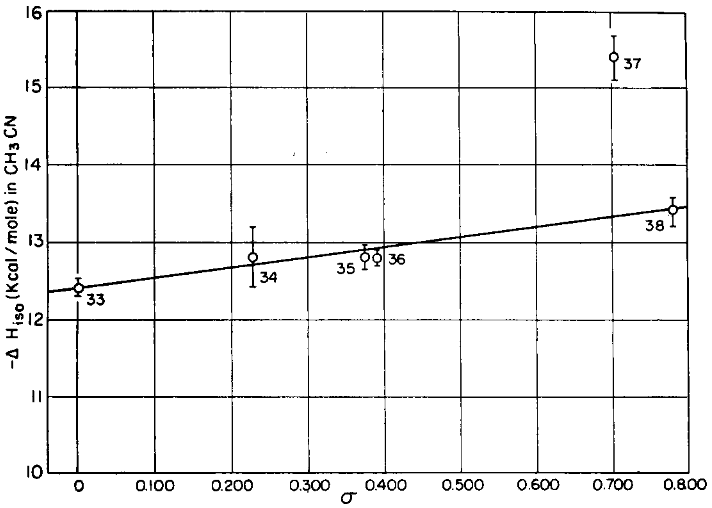

FIG. 4.— $-\Delta H_{\text{iso}}$ in acetonitrile *vs.* σ for substituted acids: (33) benzoic, (34) *p*-chlorobenzoic, (35) *m*-chlorobenzoic, (36) *m*-bromobenzoic, (37) *m*-nitrobenzoic, (38) *p*-nitrobenzoic.

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Zusammenfassung—Acetonitril als Medium für thermometrische Säure-Basen-Titrationen wurde untersucht. Sehr viele Amine und organische Säuren lassen sich befriedigend titrieren, aber die Zersetzlichkeit des Lösungsmittels in Gegenwart starker Basen begrenzt die praktische Anwendbarkeit. Es werden Neutralisationswärmen verschiedener Säuren in Acetonitril angegeben; die Ergebnisse an m- und p-substituierten Benzoesäuren entsprechen ihren Hammettschen σ-Werten.

Résumé—On étudie l'utilisation de l'acétonitrile comme milieu pour des titrages thermométriques acide-base. Les résultats sont satisfaisants pour de nombreux acides organiques et de nombreuses amines, mais l'instabilité du solvant en présence de bases fortes limite grandement son application pratique. On donne des résultats sur les chaleurs de neutralisation de différents acides dans l'acétonitrile; les résultats pour les acides benzoïques m- et p- substitués se corrèlent bien avec les valeurs de leurs σ de Hammett.

REFERENCES

[1] H. W. Linde, L. B. Rogers and D. N. Hume, *Analyt. Chem.*, 1953, **25**, 404.
[2] S. T. Zenchelsky, *ibid.*, 1960, **32**, 289R.
[3] H. J. Keily and D. N. Hume, to be published.
[4] J. S. Fritz, *ibid.*, 1953, **25**, 407.
[5] F. F. Critchfield and J. B. Johnson, *ibid.*, 1954, **26**, 1803.
[6] H. B. Van der Heijde and E. A. M. F. Dahmen, *Analyt. Chim. Acta*, 1957, **16**, 378.
[7] H. J. Keily, Thesis, Massachusetts Institute of Technology, 1956.
[8] M. Kilpatrick, *Chem. Rev.*, 1933, **13**, 131.
[9] H. J. Keily and D. N. Hume, *Analyt. Chem.*, 1956, **28**, 1294.
[10] E. J. Forman and D. N. Hume, *J. Phys. Chem.*, 1959, **63**, 1949.
[11] D. B. Bruss and G. E. A. Wyld, *Analyt. Chem.*, 1957, **29**, 232.

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POLAROGRAPHY OF COPPER IN DIETHYLENE-TRIAMINEPENTA-ACETIC ACID SOLUTIONS

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Summary—The polarographic behaviour of copper in the presence of excess DTPA has been studied by means of the dropping mercury electrode. In an acidic medium the copper^{II} complex is reversibly reduced to the amalgam. At pH values above 5 the wave is broken into two parts and a new irreversible wave appears at a more negative potential. An increase in pH of the supporting electrolyte results in an increase of the second wave at the expense of the original one, the limiting current of the total wave remaining constant. The effect of temperature, pressure of mercury, pH and the concentration of DTPA on the limiting current and the half-wave potentials of the two waves have been investigated and the stability constant of the copper-DTPA complex has been redetermined. The double wave is assumed to be the result of an inhibited electrode reaction, the inhibition being caused by the deposition of the reduction product at the electrode surface. When the applied potential is increased above $-0{\cdot}7$ V *vs.* S.C.E., the film is desorbed and the current rises to its original value.

INTRODUCTION

DIETHYLENETRIAMINEPENTA-ACETIC acid (DTPA) forms stable complexes with copper^{II}. In the presence of excess DTPA three complexes with the formulae CuH_2DTPA, CuHDTPA and CuDTPA, respectively, are formed at various pH. The complexes have been investigated by spectrophotometric and potentiometric methods and the stability constants determined.[1–4]

The polarographic behaviour of the copper-DTPA chelates has not previously been investigated. Preliminary experiments with the dropping mercury electrode (D.M.E.) showed that copper in the presence of excess DTPA is reduced in two steps in an alkaline medium, and that the ratio of the two waves was highly dependent on the pH of the supporting electrolyte. The present work was carried out in order to study this effect of pH on the reduction of the copper-DTPA complexes.

EXPERIMENTAL

Reagents

Diethylenetriaminepenta-acetic acid: Obtained from Geigy Chemical Corp., New York, U.S.A. The commercial DTPA was recrystallised twice from a minimum amount of hot water and dried in the air. The purity of the product was checked by infrared analysis. A 0·05*M* stock solution was prepared by dissolving 19·7 g of DTPA and 6 g of sodium hydroxide in distilled water and diluting to 1 litre. The solution was standardised against dipyridozincthiocyanate according to Buděšinsky.[5]

Standard copper^{II} solution: Prepared by dissolving an accurately weighed amount of electrolytic copper in nitric acid. Part of the excess acid was evaporated and the residue diluted to appropriate volume.

The remaining chemicals were of reagent grade quality and they were used without further purification.

Two-tenths molar acetate-. phosphate- and ammonia-buffers were used as supporting electrolytes. The pH of the electrolytes was adujsted to the desired value by adding hydrochloric acid or potassium hydroxide to the solution and its pH measured with a pH meter. Triton X-100, obtained from Rohm and Haas Co., Philadelphia, U.S.A., was used as maximum supressor in some experiments.

Apparatus

Polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany). The conventional type of dropping mercury electrode and of electrolysis cell was used. The capillary characteristics, measured in $0{\cdot}1M$ potassium nitrate (open circuit) at a mercury height of 52·4 cm were: $m = 2{\cdot}998$ mg/sec and $t = 3{\cdot}52$ sec. An external saturated calomel electrode (S.C.E.), connected to the cell by means of an agar bridge, served as reference electrode. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis. All experiments were performed at 25 ± 0·1°.

The reversibility of the electrode reactions was tested by determining the temperature coefficient of the half-wave potentials and the slopes of the curves of log $i/(i_d - i)$ *vs.* potential. Corrections were made for the residual current and IR-drop in the circuit. Data for the logarithmic plots were taken by manual operation of the polarograph, measuring the applied potential with a Hartman and Braun (No. 10018) potentiometer. Half-wave potentials of the reversible waves were taken from the logarithmic plots and were reproducible to ±1 mV.

RESULTS

Preliminary experiments

Current-voltage curves of DTPA in supporting electrolytes of different pH showed that the reagent is not reduced at the D.M.E. An anodic wave, however, probably from the oxidation of mercury to a mercury-DTPA complex, was observed on all polarograms. The wave was shifted to more negative values with an increasing pH of the supporting electrolyte and the height of the wave was found to be proportional to the concentration of DTPA.

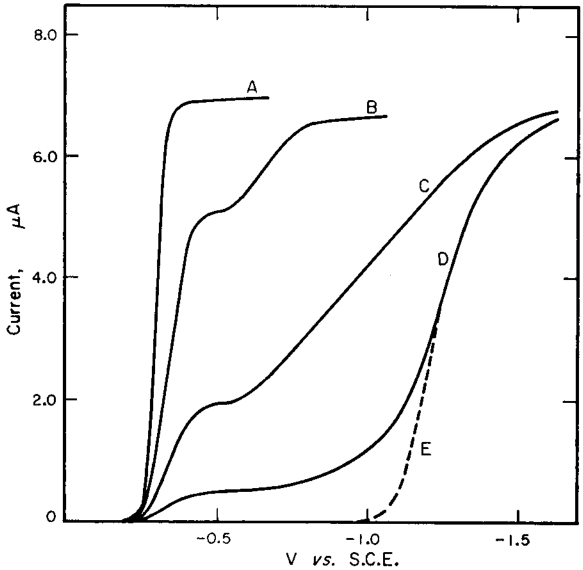

FIG. 1.—Polarograms of $10^{-3}M$ copper^{II} and $10^{-2}M$ DTPA in acetate buffer pH 4·60 with various amounts of Triton X-100 present: (a) 0%, (b) 0·002%, (c) 0·003%, (d) 0·006%, and (e) >0·01%.

Polarograms of copper in the presence of DTPA exhibited a maximum when recorded from solutions with low pH values. The maximum was easily suppressed by the addition of a minute amount of Triton X–100. Larger amounts of Triton had, however, a marked effect on the reduction wave, which was split into two waves and the limiting current was strongly decreased over a considerable potential range. A few polarograms recorded in the presence of various amounts of Triton X–100 are shown in Fig. 1. Experiments showed that the presence of 0·0005% of Triton was

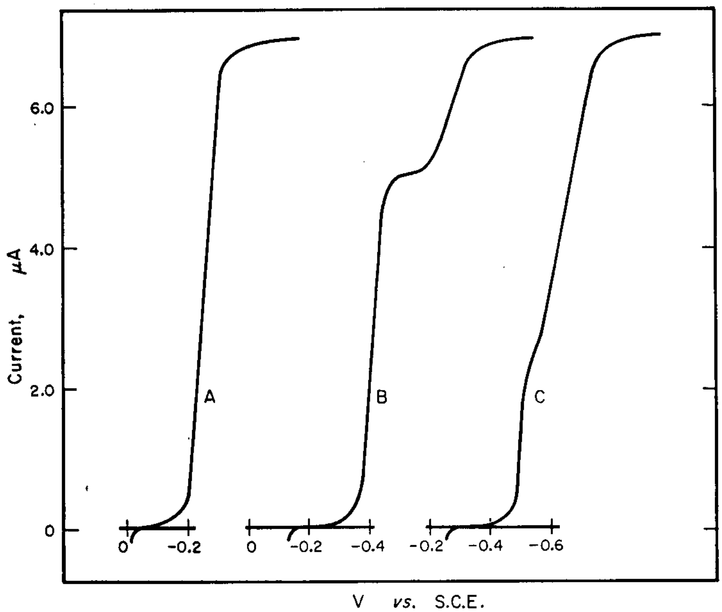

FIG. 2.—Polarograms of $10^{-3}M$ copper^{II} and $10^{-2}M$ DTPA: (A) acetate buffer pH 4·65, (B) phosphate buffer pH 6·80, and (C) phosphate buffer pH 9·60.

sufficient to suppress the maximum and this low concentration had no undesirable effect in an acidic medium. No maximum was observed on polarograms recorded from solutions with a pH greater than 4, and in the following experiments no surface active substances were added to the supporting electrolytes in the pH range 4–12.

Effect of pH

The effect of pH on the cathodic wave of copper^{II} in the presence of excess DTPA was investigated, using acetate and phosphate buffers as supporting electrolytes. Polarograms recorded from solutions with a pH less than 5 consisted of a single well-defined wave, whereas a second wave appeared on polarograms recorded at higher pH. An increase in pH of the supporting electrolyte resulted in an increase of the second wave at the expense of the first one, the total limiting current remaining constant. A few typical polarograms are shown in Fig. 2. The half-wave potential of the first wave was shifted to more negative values with increasing pH as indicated in Fig. 3. The half-wave potential of the second wave, however, remained practically constant ($E_{\frac{1}{2}}$ = —0·68 V *vs.* S.C.E.) in the entire pH range 5–12. The lower limit of pH in these measurements is restricted by the solubility of DTPA and the dissolution wave of mercury which interfered at pH values less than 3. The variation of the height of the first and second wave with the pH of the supporting electrolyte, is plotted in Fig. 4. The above results were perfectly reproducible. At a given pH identical polarograms were obtained, independent of the supporting electrolyte used (*i.e.*, acetate, phosphate or potassium nitrate/potassium hydroxide). The ratio between the first and second wave increased, however, in the presence of ammonia (Fig. 4). This is probably because of a mixed ligand complex and will be discussed below.

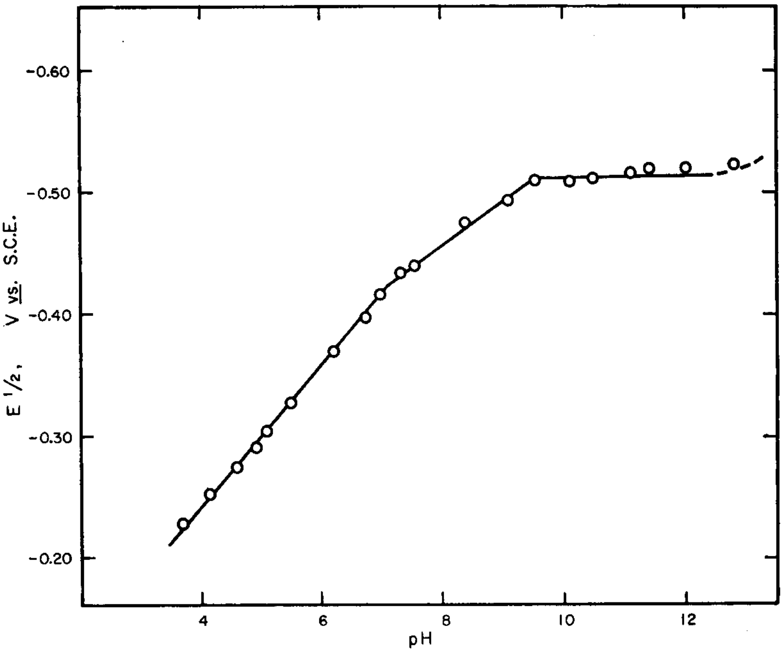

FIG. 3.—Half-wave potentials of the first wave of $10^{-4}M$ copper^{II} and $10^{-2}M$ DTPA at various pH values.

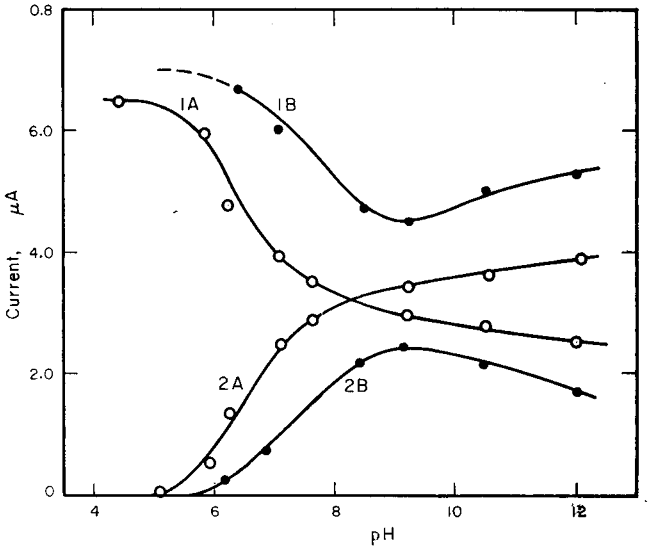

FIG. 4.—Limiting currents of the first (1) and second (2) wave of $10^{-3}M$ copper^{II} and $10^{-2}M$ DTPA at various pH values: (A) acetate and phosphate buffers, (B) ammonia buffers.

Reversibility of the electrode reactions

The reversibility of the electrode reactions was tested by plotting log $i/(i_d - i)$ *vs.* the potential. The plots yield straight lines at all pH for the first wave, and the slope of the lines indicated a reversible two-electron reduction of copper to the amalgam.

The half-wave potential of the first wave shifted to more negative values with an increasing concentration of DTPA, and the plot of the values of $E_{\frac{1}{2}}$ *vs.* the corresponding values of log C_x, resulted in straight lines. The slope of the lines indicated that only one group is co-ordinated in the complex. In the concentration range 5×10^{-4} to $10^{-2}M$ DTPA, the half-wave potential of the first wave may be expressed by the equation:

$$E_{\frac{1}{2}} = -0{\cdot}576 - 0{\cdot}029 \log C_x.$$

The concentration C_x of the free ligand available for complex formation was calculated using the dissociation constants of DTPA reported by Anderegg and coworkers.[2]

The second wave, which appeared on polarograms recorded from solutions with a pH greater than 5, showed an irreversible reduction. The plot of log $i/(i_d - i)$ *vs.* the potential yields curved lines at all pH from 5 to 12. The half-wave potential of this wave, taking $E_{\frac{1}{2}}$ as the point on the curve where $i = i_d/2$, was constant (—0·68 V *vs.* S.C.E.) and independent of the pH of the supporting electrolyte and the excess of DTPA present.

Effect of temperature

The effect of temperature on the cathodic waves of copper in the presence of excess DTPA was tested in acetate and phosphate buffers. In the region 20–45° the temperature dependence of both the half-wave potential and the height of the first wave was linear. The temperature coefficient of the half-wave potential, —0·3 mV/degree, is of the proper sign and magnitude for that of a reversible process.

TABLE 1.—EFFECT OF TEMPERATURE

Temp., °*C*	First wave		Second wave	
	$-E_{\frac{1}{2}}$, *V*	Current, *μA*	$-E_{\frac{1}{2}}$, *V*	Current, *μA*
20	0·396	0·53	0·68	0·16
25	0·397	0·56	0·68	0·16
30	0·399	0·60	0·68	0·16
35	0·400	0·64	0·68	0·16
40	0·402	0·68	0·68	0·15
50	0·403	0·73	0·68	0·15

$10^{-4}M$ copper^{II} and $10^{-2}M$ DTPA in phosphate buffer of pH 6·60.

The temperature coefficient of the diffusion current was 1·3% per degree, indicating a diffusion-controlled process. The data obtained from phosphate buffer pH 6·6 are reported in Table I. At this pH the two waves are very well separated and the temperature dependence of the second wave could also be measured. As seen from the table, the half-wave potential and the height of the second wave were found to be independent of the temperature within the experimental error.

Diffusion current constant

The diffusion current constant at different pH was determined by measuring the limiting current of 2×10^{-5} to $2 \times 10^{-3}M$ copper in the presence of $10^{-2}M$ DTPA. In the pH range 3–10, using acetate and phosphate buffers as supporting electrolytes, the limiting current of the *total wave* was independent of pH and it increased proportionally to the concentration of copper at all pH. The diffusion current constant in these media was found to be $I = 2{\cdot}42 \pm 0{\cdot}06$. In ammonia buffers of pH 10–12 the diffusion current constant was somewhat larger, $I = 2{\cdot}55 \pm 0{\cdot}05$. Comparison of these values with the diffusion current constant of the copper EDTA-complex determined by Pecsok,[6] $I = 2{\cdot}85$, indicates that the total wave is caused by a two-electron reduction of copper to copper amalgam.

Effect of drop time

The effect of drop time was investigated by recording polarograms of $10^{-4}M$ copper and $10^{-2}M$ DTPA in acetate and phosphate buffers at various heights of the mercury column. The height of the single wave obtained at pH <5 and the first wave obtained at higher pH values, increased with the height of the mercury; the value $i/\sqrt{h}$, where h is the height of the column after correction for the "back-pressure", was constant, indicating that the electrode reaction is diffusion controlled. The height of the second wave was found to increase proportionally to the height of the mercury column and indicates that this wave is from an adsorption on the electrode and that the current is controlled by the rate of penetration of the copper complex through an adsorbed film.[7] The data obtained at pH 6·65 are given in Table II.

TABLE II.—EFFECT OF PRESSURE OF MERCURY

$h_{corr.}$, *cm*	First wave		Second wave	
	i_d, μA	$i_d/\sqrt{h_{corr.}}$	i, μA	$i/h_{corr.}$
45·6	4·65	0·69	1·40	0·031
50·6	4·95	0·68	1·55	0·031
55·6	5·15	0·69	1·70	0·031
60·6	5·35	0·68	1·85	0·031

$10^{-3}M$ copper^{II} and $10^{-2}M$ DPTA in phosphate buffer of pH 6·65.

The drop time of the capillary was also measured as a function of the applied potential. The electrocapillary maximum was not shifted and the general shape of the curve did not change upon the addition of $10^{-3}M$ copper and $10^{-2}M$ DTPA to the supporting electrolyte, but a 2% decrease in drop time was observed over a considerable potential range.

DISCUSSION

It is evident from the experimental data that the first wave is from a reversible, diffusion-controlled, two-electron reduction of the copper-DTPA complex. The observed half-wave potentials are linear functions of the pH in the regions 4–7, 7–10 and 10–12·5 (Fig. 3). The slopes of the curves are —0·060, —0·035 and 0

V/pH unit, respectively, indicating that the following reactions take place at the electrode:

$$CuA^{3-} + 2H^+ + 2e^- \xrightarrow{pH\,4-7} Cu(Hg) + H_2A^{3-}$$
$$CuA^{3-} + H^+ + 2e^- \xrightarrow{pH\,7-10} Cu(Hg) + HA^{4-}$$
$$CuA^{3-} + 2e^- \xrightarrow{pH\,10-12{\cdot}5} Cu(Hg) + A^{5-}$$

where H_5A represents DTPA.

At pH <4, the conditional constant[4] of $CuHA^{2-}$ is of the same order as that of CuA^{3-}, and the following reaction will probably take place in that pH region:

$$CuHA^{2-} + 2H^+ + 2e^- \xrightarrow{pH<4} Cu(Hg) + H_3A^{2-}.$$

The stability constants of the CuA^{3-} complex, calculated from the half-wave potentials of the first wave, was $pK_c = 20{\cdot}4$. Considering the great difference in ionic strength, this value compares favourably with the values 21·0, 21·5, 21·1 and 20·5 previously determined by potentiometric titration.[1–4]

The interpretation of the second wave is more difficult. The half-wave potential of this wave was constant, independent of excess reagent, pH and the kind of supporting electrolyte. Consequently, the double wave is not from the reduction of two copper complexes of different composition or mixed ligand complexes. The effect of temperature and the height of the mercury column on the second wave, indicates that the current is controlled neither by diffusion nor by kinetic reactions. At a given pH, the height of the second wave is proportional to the concentration of copper and to the height of the mercury column. The current did not, however, reach a limiting value with increasing concentration as in the case of catalytic and classical adsorption waves.

The double wave may, however, be the result of an inhibited electrode reaction.[8,9,10] The DTPA liberated at the electrode during the electrolysis is therefore assumed to be surface active and to accumulate on the electrode surface during the life of the drop. The effect will then be similar to the addition of Triton (Fig. 1), and the reaction will be partly inhibited until the desorption potential is reached. When the applied potential is increased above this value (about —0·7 V *vs.* S.C.E.), the film is desorbed and the current will rise to its original value.

Equipment for oscillographic current/time curves[8] was not available in this laboratory, but a detailed inspection of undamped polarograms indicated that an inhibition mechanism occurred at the electrode and the height of the second wave increased proportional to the height of the mercury column, as in the case of limiting penetration currents.[7]

At a given pH value the ratio of the two waves, and hence the degree of inhibition, was found to be independent of excess DTPA in the solution, indicating that only the DTPA species liberated at the electrode during the electrolysis is surface active. Hence, the electrode reaction cannot be completely inhibited as by the addition of a large amount of Triton X–100 (Fig. 1). The DTPA anions are desorbed at a less negative potential (—0·7 V) than the neutral Triton X–100 molecule (—1·3 V), indicating that the desorption potential depends on the charge and type of inhibitor present in the electrolyte.

It is of interest to note that the second wave does not appear on polarograms recorded from solutions of pH less than 5. In this pH range H_3A^{2-} is formed during the reduction and is probably less surface active and not so strongly adsorbed as the HA^{4-} and A^{5-} species liberated at higher pH values.

The co-ordination number of copper is six in the copper-EDTA complex and according to Kirson and Citron the complex exists as a polymer in solution.[11] By the addition of ammonia to the solution, the polymer is disrupted into single

$$[Cu(NH_3)_2EDTA]^{2-}$$

units.[12] A similar polymer with hexaco-ordinated copper is probably also formed in DTPA solutions, the six co-ordination being completed by weak intermolecular $C=O\cdots Cu$ linkages. When ammonia or ethylenediamine was added to the copper-DTPA chelate in phosphate buffer of pH 9–12, the blue colour of the complex increased in intensity. Polarograms of these solutions exhibited two waves as in phosphate buffers, but the height of the first wave increased at the expense of the second one upon addition of ammonia or polyamines to the supporting electrolyte, whereas the half-wave potentials remained practically constant. At a given pH and excess ammonia or ethylenediamine, the ratio of the two waves was constant and independent of other electrolytes present (Fig. 4). These experiments indicate that the DTPA species liberated at the electrode is less surface active and that a smaller amount is adsorbed in the presence of ammonia. It is possible that this effect is caused by a disruption of the polymer and the formation of a mixed ligand complex similar to that in EDTA solutions. No mixed ligand DTPA complexes have yet been reported in the literature, but the existence of a copper-ammonia–DTPA complex may probably be verified by infrared experiments as in the case of the EDTA complexes.[11,12]

Zusammenfassung—Das polarographische Verhalten von Kupfer in Gegenwart von überschüssiger DTPA wurde an der Quecksilbertropfelektrode untersucht. In saurem Medium wird der Kupfer (II)-Komplex reversibel zum Amalgam reduziert. Bei p_H-Werten über 5 spaltet die Welle in zwei auf und eine neue irreversible Welle erscheint bei negativerem Potential. Ansteigen des p_H des Leitelektrolyten läßt die zweite Welle auf Kosten der ersten ansteigen, wobei der Gesamt-Grenzstrom konstant bleibt. Der Einfluß von Temperatur, Quecksilberdruck, p_H und DTPA-Konzentration auf Grenzstrom und Halbwellenpotential der beiden Wellen wurden untersucht und die Stabilitätskonstante des Cu-DTPA-Komplexes neu bestimmt. Die Doppelwelle wird als Folge einer gehemmten Elektrodenreaktion gedeutet, wobei die Hemmung in der Abscheidung des Reaktionsproduktes an der Elektrodenoberfläche besteht. Wenn die angelegte Spannung über −0,7V gegen die gesättigte Kalomelektrode gesteigert wird, wird der Film desorbiert, und der Strom steigt auf seinen ursprünglichen Wert an.

Résumé—Le comportement polarographique du cuivre en présence d'un excès de DTPA (acide diéthylène triamine pentaacétique) a été étudié au moyen de l'électrode à gouttes de mercure. En milieu acide le complexe du cuivre(II) est réduit réversiblement en amalgame. A un pH supérieur à 5 la vague se dédouble et une nouvelle vague irréversible apparaît à un potentiel plus négatif. A une augmentation de pH de l'électrolyte support correspond une augmentation de la hauteur de la deuxième vague aux dépens de la vague initiale, la somme des courants de diffusion restant constante. L'effet de la température, de la pression du mercure, du pH et de la concentration de DTPA sur le courant de diffusion et sur les potentiels de demi-vague des deux vagues a été étudié et la constante de stabilité du complexe Cu-DTPA a été déterminée à nouveau. La double vague est supposée être le résultat d'une réaction à l'électrode inhibée, cette inhibition étant due au dépot du produit de réduction sur la surface de l'électrode. Quand le potentiel appliqué devient plus négatif que −0,7 V/E.C.S le film est désorbé et le courant reprend sa valeur initiale.

REFERENCES

[1] E. Durham and D. Ryskiewich, *J. Amer. Chem. Soc.*, 1958, **80**, 4812.
[2] G. Anderegg, P. Nägeli, F. Müller and G. Schwarzenbach, *Helv. Chim. Acta*, 1959, **42**, 827.
[3] S. Chaberek, A. E. Frost, M. A. Doran and N. J. Bicknell, *J. Inorg. Nuclear Chem.*, 1959, **11**, 184.
[4] E. Wänninen, *Acta Acad. Aboensis, Math. Phys.*, 1960, XXI, 17.
[5] B. Buděšinsky, *Coll. Czech. Chem. Comm.*, 1956, **21**, 255.
[6] R. L. Pescok, *Analyt. Chem.*, 1953, **25**, 561.
[7] T. Biegler, *J. Electroanalyt. Chem.*, 1962, **4**, 317.
[8] R. W. Schmid and C. N. Reilley, *J. Amer. Chem. Soc.*, 1958, **80**, 2087.
[9] H. W. Nürnberg and M. von Stackelberg, *J. Electroanalyt. Chem.*, 1962, **4**, 1.
[10] P. R. Subbaraman, P. S. Shetty and J. Gupta, *Analyt. Chim. Acta*, 1962, **26**, 179.
[11] B. Kirson and I. Citron, *Bull. Soc. chim. France*, 1959, 365.
[12] I. Citron, *Analyt. Chim. Acta*, 1962, **26**, 446.

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GEOMETRY-RELATED ERRORS IN INSTRUMENTAL NEUTRON-ACTIVATION ANALYSIS

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Summary—Geometry-related errors in instrumental neutron-activation analysis are defined and evaluated. Neutron-flux distributions, variations in counting geometry, and intra-sample neutron moderation and reflection are discussed in relation to these errors. Devices for error control are described.

NEUTRON ACTIVATION when combined with γ-ray spectrometry and decay-rate analysis offers a purely instrumental, non-destructive approach to elemental analysis. Because of the high penetrativeness of neutrons and of γ-rays, matrix effects are exceptionally small. In many cases, samples as large as 25–30 ml are analysed. Furthermore, in most cases, the results are relatively insensitive to differences in composition, sample volume or bulk density. With the introduction of accelerator systems for neutron production, this method, called instrumental neutron-activation analysis here, comes within the budgetary, space and manpower limitations of many laboratories, and shows promise of taking a place among the established instrumental analytical tools of the modern laboratory.

The physical concepts of the method, its instrumentation and some typical applications to routine analyses have been presented by Guinn and Wagner[1] for the system used in the Emeryville Research Center of Shell Development Company. Using this system, Guinn and Johnson[2] have found instrumental neutron activation to be a reliable and convenient tool for routine analysis and to be especially valuable in quickly solving new or unusual analytical problems which by other methods would require considerable research and development.

In seeking the greatest power and efficiency for this new method, it is the task of analytical research and development to explore its variables systematically and to relate them to such analytical characteristics as sensitivity, precision and selectivity. As a part of this exploration, the present study has to do with errors related to sample-source geometry and to sample-counter geometry. In the typical activation determination, results are calculated on the basis of a comparison of the respective count rates of a sample and a standard. Implicit in this comparison are the assumptions that sample and standard are exposed to the same neutron flux and are counted with the same counting efficiency. In practical activation sources, however, the neutron-flux distribution is non-uniform, and presents significant differences between and within sample spaces. Furthermore, for the detectors and samples used, the counting efficiency varies significantly over the sample space. Thus the assumptions of constant flux and constant counting efficiency are not simply and exactly met. In an evaluation of the analytical consequences of this situation, this study presents surveys of neutron distributions and of counting efficiencies, relates these variables to certain errors in activation analysis, and describes methods for control of these errors.

Although the results are specific for the actual source used, the principles evolved and the approach taken to control the geometry-related errors are expected to be generally applicable to other systems for instrumental neutron-activation analysis.

EXPERIMENTAL

Apparatus

Neutron source: The neutron source used is a modification of the source described by Guinn and Wagner[1] and illustrated in Fig. 1. Neutrons are generated by the action of bremsstrahlung, from a 3-MeV Van de Graaff electron accelerator with a gold target, on beryllium in a 6-inch cube of the metal. The moderator is Santowax, a radiation-resistant wax. Neutron shielding is accomplished by a Boral cover and by boric acid around the side and bottom of the assembly.

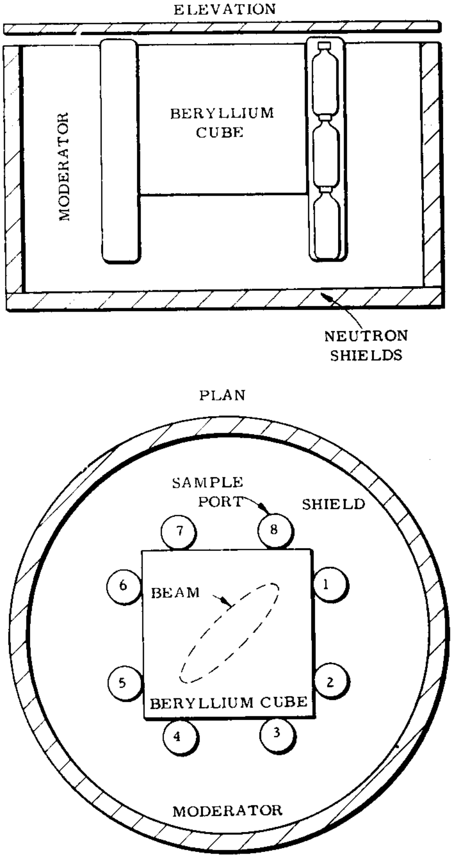

FIG. 1.—The photoneutron source.

Scintillation counter: Well-type NaI(Tl) crystal is used to yield maximum counting efficiency and to achieve the smallest variation in counting geometry with sample volume. The well accommodates commercially available 1-oz polyethylene bottles, as shown in Fig. 2. The over-all dimensions of the crystal, diameter × depth, is 3″ × 3″.

Procedure

Flux-distribution patterns are determined by activating and counting gold foils (usually about 20 mg of 0·5 mil gold sheet) supported in appropriate positions on pressure-sensitive cellophane tape.

The position of the X-ray beam relative to the beryllium block is determined photographically with the aid of X-ray sensitive polyvinyl chloride sheet.[3]

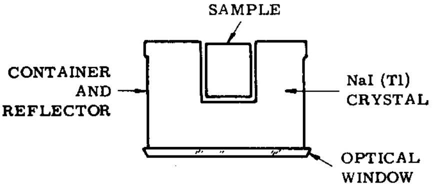

FIG. 2.—Cross-section of scintillation well detector with sample in well.

The neutron-flux levels in different sample ports are determined by activating and counting a set of nearly identical standards, *e.g.*, gold foils, or suitable solutions, such as 0·1% manganous nitrate, at a given level in sample ports around the core.

Volume effects and height effects are determined in an analogous way using monitors irradiated and counted under the conditions being tested.

RESULTS AND DISCUSSION

Positioning errors

Positioning errors are defined as errors attributable to differences in neutron flux at a given level from sample port to sample port. A typical positioning error pattern is given in Fig. 3. Also shown in this figure is the corresponding beam-to-core orientation, according to the photograph for this positioning run. A comparison of the pattern and the diagram illustrates the main dimensional and geometric effects on the pattern. In particular, positions 5–8 show a generally higher flux than positions 1–4, which correlates with the beam being located closer to the former positions than to the latter. Furthermore, a geometric correlation is observed in the similarity of the pattern for positions 1–4 to that for positions 4–8; thus the symmetry of the beam scan is reflected in the symmetry of the positioning pattern.

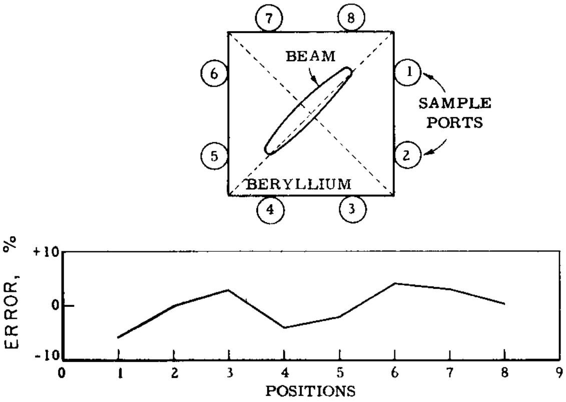

FIG. 3.—Positioning error with an uncentred beam.

The correlations observed above are generally found throughout a series of positioning runs. However, the variability of the patterns from run to run is great enough to reduce the value of any single pattern as a calibration standard.

The position-to-position variation and the run-to-run variability are largely attributed to the strong dependence of the neutron flux on beam-to-sample distance. An illustration of this effect is given in Fig. 4, which presents the changes in neutron flux in the sample space with changes in the distance from the beam centre to the sample (see inset in Fig. 4). According to Fig. 4, the gradient for the centred beam, *i.e.*, at a beam-sample distance of 3·5 inches, is 16–20 relative % per inch. For a beam which is 0·25 inch off centre, this gradient corresponds to a difference of 8–10% between fluxes in ports on opposite sides of the core and, therefore, yields a positioning pattern like that of Fig. 3. In terms of precision, the above effects yield an error component of about 3% relative standard deviation.

Another view of the effect of flux distribution is given in Fig. 5, which shows how the flux varies with distance from the beam axis for a centred beam (see inset in Fig. 5).

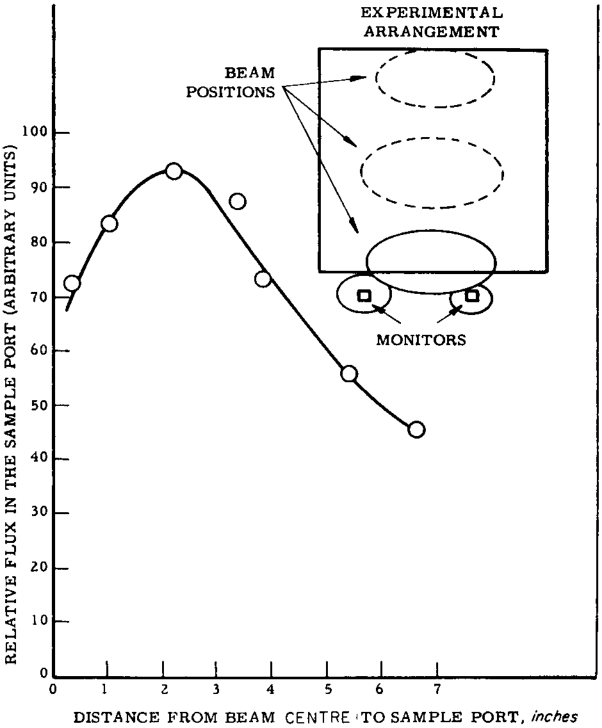

FIG. 4.—Effect of beam-to-port distance of flux in the sample port (beam position variable).

The sharp flux-distance gradient has the same implications as in the preceding discussion. A small maximum in the flux distribution is found in the reflector near its interface with the core. This maximum, signifying a local accumulation of neutrons in the reflector, is attributed to the fact that in comparison with the beryllium of the core the wax moderator has greater moderating power and a smaller neutron capture cross section.[4] The distribution of Fig. 5 is measured at the top of the source, *i.e.*, above the level of Sample C in Fig. 1. Experimental determination of distributions at lower levels are not feasible in this system, but results from other systems, to be described elsewhere, indicate that maxima at lower levels are less sharp. The development of the maximum near the interface has the effect of reducing the error from inhomogeneity within a cross-section of the sample.

Devices for controlling the positioning error

Foil monitors. Flux monitors of gold foil are attached to the tops of the containers of samples and standards, carried through the irradiation, and counted to yield a position-to-position flux calibration for the respective irradiation. Use of monitors is simple, but it contributes an additional counting error to the result.

"Lazy susan" sample rotation. If the sample ports and core are radially symmetrical with respect to an axis, rotation of samples about that axis eliminates errors from beam wandering and core-to-beam eccentricity. In practice, some variation is usually found from position-to-position because of dissymmetries in the rotating assembly, *i.e.*, in the interrelationship of ports, core, and axis of rotation. However, if the axis of rotation is accurately centred with respect to the ports, the pattern of flux variation from these dissymmetries is reproducible and, once determined, may be used as a calibration curve.

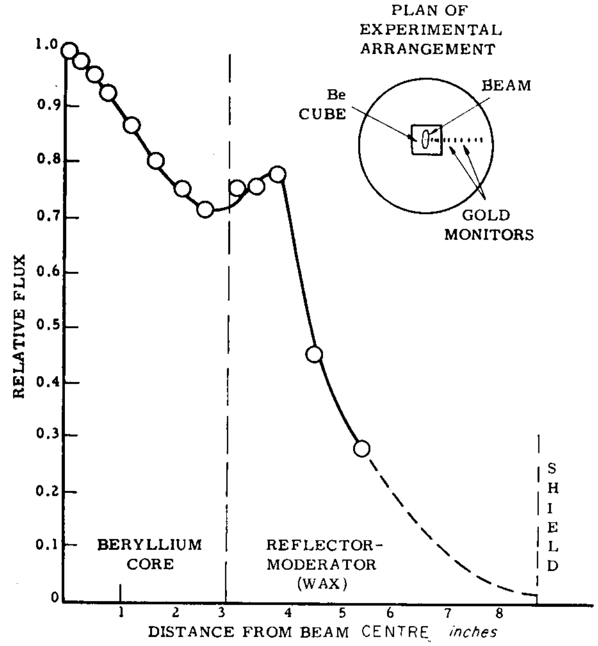

FIG. 5.—Effect of beam-to-monitor distance of flux distribution transverse to the beam (beam position fixed).

The off-centre beam position. If only one sample and one standard are to be irradiated, excellent flux uniformity can be achieved by scanning the beam parallel to and about 1 inch from one edge of the core, as shown by the beam position with the solid outline in Fig. 4. In this beam-to-core orientation, two effects compensate each other to form a maximum in the plot of flux available to the sample *vs.* beam-to-port distance as shown in Fig. 4. The compensating effects which result in the maximum are (1) a decrease in flux with increase in beam-to-port distance resulting from inverse square attenuation and neutron capture and (2) an increase in flux with increase in beam-to-port distance because of an increase in the fraction of bremsstrahlung beam falling within the beryllium core.

Volume errors

The volume errors in this discussion are those errors in activation analysis attributable to differences between the volumes of samples and the volumes of their respective comparison standards. In this investigation of these errors, the variables studied are: (1) differences in neutron flux at different levels within the ports, (2) enhancement of intra-sample neutron flux with increase of sample volume, and (3) differences in counting efficiency at different levels in the detector well.

The relationship between neutron flux and height within the sample port is shown in Fig. 6. The three sample positions indicated in Fig. 6 correspond with the sample levels shown in Fig. 1, the diagram of the neutron source assembly. It is evident from Fig. 6 that the neutron flux available to the sample depends strongly on the height at which it is situated in the sample port. It is also evident that both the sign and magnitude of the intra-sample flux-to-height gradient depend strongly on the choice of height at which the sample is irradiated. For example, for a sample in position A or position B of this source, the neutron flux increases with increasing height, *cf.*, Curve 1, Fig. 7; however, for a sample in position C, the neutron flux decreases with increasing height.

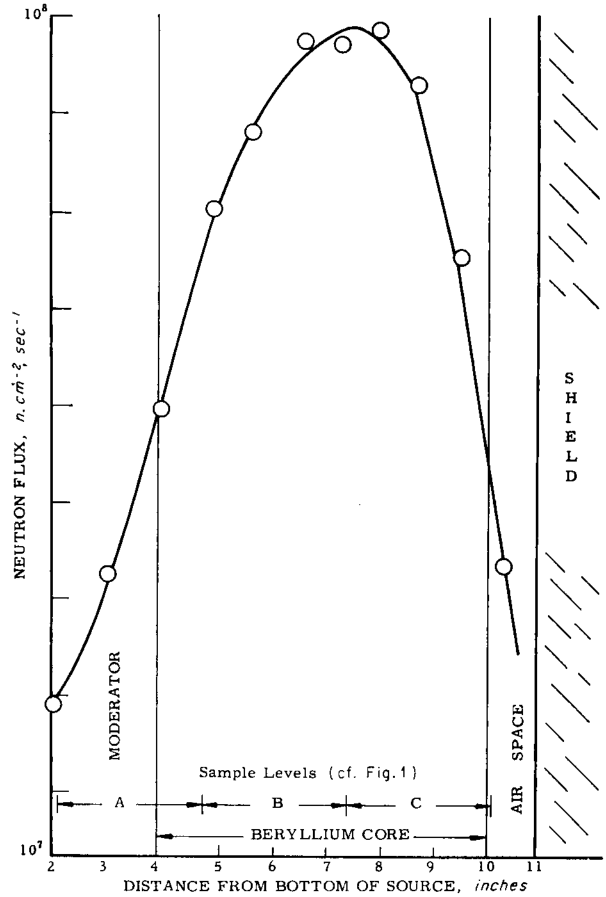

FIG. 6.—Flux distribution parallel to the beam axis (vertical distribution).

In instrumental neutron-activation analysis, the counterpart of the flux-to-height variation is the variation of counting efficiency with height in the detector. The latter relationship, shown in Curve 2 of Fig. 7, is largely determined by the sample-well geometry.

The count rate measured in a practical activation analysis, which is called the activation count rate here, is a function of the product of the neutron flux and the counting efficiency. Correspondingly, the variation of activation count rate with height in a given sample space varies with the product of the respective flux- and counting efficiency-height variations. This inter-relationship is illustrated in Fig. 7 for irradiation in the B position of the present source (Figs. 1 and 6). In this situation, the height-flux gradient (Curve 1, Fig. 7) is opposite in sign, but nearly equivalent in magnitude to the height-counting efficiency gradient (Curve 2, Fig. 7). Thus these two effects in an activation analysis may approximately cancel each other to yield a relatively small dependence of activation-induced count rate on height, as shown in Curve 3, Fig. 7. However, a quite different relationship may be found for irradiations carried out at a different height in the sample port. For example, samples irradiated in the C-position of the present source (Figs. 1 and 6) are exposed to a neutron flux which decreases with increasing height in the port. In this situation the flux-height gradient and the counting efficiency-height gradient enhance each other to yield a relatively strong dependence of activation count rate on sample height. It is clear, therefore, that the magnitude of errors possible from discrepancies between respective sample and standard volumes varies widely with differences in the height at which irradiations are carried out.

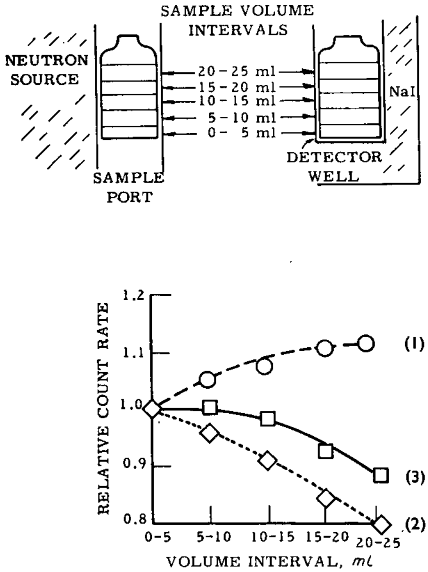

FIG. 7.—Intra-sample height effects for the B-level sample space of Fig. 6.
Above: Diagram of intra-sample volume segments.
Below: Data plots for total counts from ^{24}Na γ-rays.
○—Variable height in source: constant height (0–5 ml) in counter.
◇—Variable height in counter: constant height (0–5 ml) in source.
□—Activation count-rate *vs.* volume interval: samples irradiated and counted in same volume interval.

The preceding discussion deals with changes accompanying the displacement of a small volume segment along the vertical axis of the counter well and/or the sample port of the neutron source. On the basis of these effects, estimates may be made of the corresponding changes accompanying increases in sample volume. These estimates may be obtained by calculating the averages of the effects for the respective small volume displacements, *e.g.*, the counting efficiency of a 10-ml sample is approximately the average of the counting efficiencies of the 0–5 ml segment and the 5–10 ml segment in the crystal well. Thus the effect of increasing volume on activation count rate may be estimated as the averages of the activation count rates for the appropriate small volume segments. For the results given in Curve 3, Fig. 7, these averages are given in Column 2, Table I. For comparison, the experimentally-determined count rates for the indicated sample volumes are given in Column 3 of this Table. The results in these two columns reveal that with increasing sample volume the experimental count rates exceed by progressively greater amounts the rates based on experiments with small volume segments. This difference is attributed to a third factor in the volume effect, namely, the effect of flux enhancement with increasing volume from intra-sample neutron moderation and reflection. This effect is more specifically demonstrated by the experiment and results shown in Fig. 8. Here it is shown that an increase in activation count rate is obtained in a sample segment without changing its radiation position or counting position if the sample segment is flanked by segments of water as a reflector. This enhancement, as indicated above, is attributed to neutron moderation and reflection within the sample. In general, the magnitude of this effect for samples ranging in volume from 2–25 ml is smaller than the flux-height and counting efficiency-height effects. Nevertheless, it is important enough to be considered in setting up the irradiation geometry for activation analysis of samples varying over a wide volume range such as this.

TABLE I.—EFFECT OF SAMPLE VOLUME ON SPECIFIC COUNT RATE OF ^{24}Na γ-RAYS IN INSTRUMENTAL ACTIVATION ANALYSIS
Samples are irradiated in the position indicated as "B" in Fig. 1 and 6 and counted in a well-type scintillation detector

Sample volume, *ml*	Relative specific count rates: Averages of rates from corresponding 5-ml segments. Results of Curve 3, Fig. 7	Relative specific count rates: Experimental rate for volume indicated
5	1·00	1·00
10	1·00	1·02
15	0·99	1·03
20	0·98	1·03
25	0·96	1·04

A similar effect observed in activation analysis in the ORNL graphite reactor is described by Reynolds and Mullins[5] as a neutron perturbation attributable to enhancement of the thermal flux by moderation of epithermal neutrons within the sample.

By using the above considerations as guide lines in choosing the irradiation positions in the present activation system, good uniformity of specific count rate over a relatively large volume range, 5–25 ml, has been obtained. This uniformity is evident in the results of Column 3, Table I. Although the examples given here are from one neutron source and one detector, the principles and general approach described have usually been successful in analyses with other neutron sources, *e.g.*, sources with beryllium cores of other shapes and sizes and fast neutron sources using the deuterium-tritium reaction to produce 14-MeV neutrons.

It should be noted that volume effects other than those which are geometry-related exist, and may cause large errors. These other effects are principally radiation absorption effects, *i.e.*, variations in self-shielding of neutrons and self-absorption of β rays and γ rays with variation in sample volume. These effects will be described elsewhere.

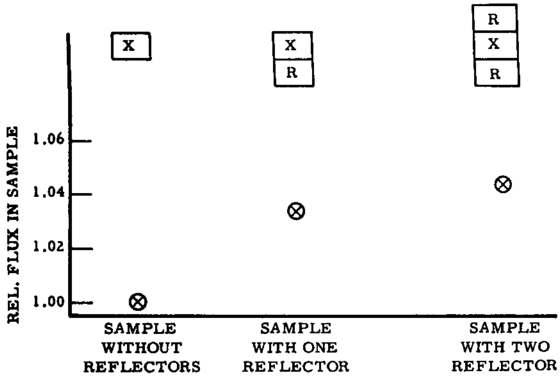

FIG. 8.—Effect of intra-sample neutron reflection.
Boxes show sample(X)-reflector(R) arrangements. For the samples irradiation position and counting geometry are held constant.

CONCLUSIONS

Geometry-related errors in instrumental neutron activation analysis are of two types, *viz.*, positioning errors and volume errors. Positioning errors are those which arise if samples and their comparison standards yield different specific count rates because of a variation in neutron flux from port-to-port around the source. In studies of this error, the port-to-port flux variations are found to correlate with small variations in beam-to-port distance. Furthermore, considerable variability among port-to-port flux patterns is found as small accidental changes in the beam-to-source geometry are made from run to run. These effects are attributed to the relatively large flux gradients shown to exist in neutron flux distributions normal to the beam axis. In the control of the positioning error, port-to-port flux patterns are usually too variable to permit the use of a single pattern as a calibration standard. However, satisfactory results have been obtained by (1) using gold foils attached to each container as flux monitors; (2) rotation of samples about the beam axis on a "lazy susan" to produce a uniform average flux to the samples; or (3) irradiation in an off-centre beam position chosen to yield excellent flux uniformity to a single sample-standard pair.

Volume errors are those which arise if the specific count rates of sample and standards are different because of differences in their volumes. The effects found to be the sources of geometry-related volume errors are the following:

(1) variation in counting efficiency with height in the detector well, which is found to be in general agreement with the variation predicted on the basis of solid geometry;

(2) variation in neutron flux with height in the port of the neutron source, which is characterised by a maximum flux near the midline of the core; and

(3) enhancement of neutron flux with increase in sample thickness, which is smaller than the preceding effects and is attributed to intra-sample neutron moderation and reflection.

From surveys of these effects on a particular system, an optimum irradiation position may be chosen in which respective height gradients compensate each other so as to yield a minimum variation of activation-induced count rate with changing volume.

This approach to control of the volume error is especially important in analysis in which large volume ranges are involved, *e.g.*, 2–25 ml. The principles and methods are expected to be applicable to instrumental activation analyses with other source-counter combinations.

Zusammenfassung—Geometrisch bedingte Fehler bei der Neutronenaktivierungsanalyse werden definiert und berechnet. Neutronenfiußverteilung, Veränderungen der Zählgeometrie und Bremsung und Reflexion von Neutronen in der Probe werden in Bezug auf diese Fehler diskutiert. Vorrichtungen zur Fehlerkontrolle werden angegeben.

Résumé—On définit et évalue les erreurs dues à la géométrie des instruments dans l'analyse par activation neutronique. On discute la distribution du flux de neutrons, la variation de la géométrie de comptage, la modération et la réflection des neutrons à l'intérieur de l'échantillon. On décrit des dispositifs pour contrôler les erreurs.

REFERENCES

[1] V. P. Guinn and C. D. Wagner, *Analyt. Chem.*, 1960, **32**, 317.
[2] V. P. Guinn and R. A. Johnson, *Trans. Amer. Nuclear Soc.*, 1960, **3**, 414.
[3] Charles Artandi and A. A. Stonehill, *Nucleonics*, 1958, **14**, May, No. 5, 118.
[4] Samuel Glasstone and Milton C. Edlund, *The Elements of Nuclear Reactor Theory*. D. Van Nostrand Co., New York, 1952, p. 247.
[5] S. A. Reynolds and W. T. Mullins, *J. Appl. Radiation and Isotopes*, 1963, **14**, 427.

Talanta, 1964, Vol. 11, pp. 159 to 173. Pergamon Press Ltd. Printed in Northern Ireland

BIVALENT THALLIUM AND THE MECHANISM OF THE ELECTRODE REACTION $Tl^{3+} + 2e \rightleftharpoons Tl^{+}$*

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Summary—The thallium^{I}-thallium^{III} electrode reaction has been studied by hydrodynamic voltammetry at platinum anodes and cathodes. Conclusive evidence is presented that the electro-oxidation of the aquo ion Tl^{+} and the electroreduction of Tl^{3+} proceed via a bivalent thallium species. Thallium^{II} is a stronger oxidant than thallium^{III} ion. In $1M$ aqueous perchloric acid the rate of the disproportionation process

$$2Tl^{II} \rightarrow Tl^{+} + Tl^{3+}$$

is relatively fast compared to the electron transfer steps

$$Tl^{II} + e \rightarrow Tl^{+}$$
$$Tl^{3+} + e \rightarrow Tl^{II}.$$

THE investigation described below was devoted to the heterogeneous electron-transfer process

$$Tl^{3+} + 2e \leftrightharpoons Tl^{+} \tag{1}$$

occurring at a platinum indicator electrode in a $1M$ aqueous perchloric acid supporting electrolyte, where the aquo-ions of univalent and tervalent thallium are the overwhelmingly predominating stable species. In view of this situation, equation (1) is of fundamental significance, as a possible example of a "single-stage two electron transfer" mechanism in an electrode reaction. In terms of a corresponding physical picture, this implies that the transfer of both electrons be completed during a single vibrational transition of the activated complex, *i.e.*, within a time interval of the order of 10^{-13} sec. For "purely chemical" electron-transfer processes occurring in homogeneous solution (*e.g.*, electron exchange between tagged and untagged ions involving two oxidation states of the same element; "cross reactions" involving two different couples, such as the oxidation of chromium^{II} by cobalt^{III}) this question has been the subject of a historic controversy. On the one hand, the Haber-Weiss school argued *a priori* that *all* electron transfer processes must necessarily be resolvable into ultimate "single electron transfer steps";[2,3] on the other hand, experimental evidence to the contrary was adduced.[4] As far as the thallium^{III}-thallium^{I} couple in perchloric acid is concerned, rate studies of the homogeneous electron-exchange process

$$Tl^{+} + \overset{*}{T}l^{3+} \xrightarrow{\text{aq. HClO}_4} Tl^{3+} + \overset{*}{T}l^{+} \tag{2}$$

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* Based on a doctoral thesis by H. A. C. The senior author (J. J.) has had the benefit of the inspired guidance of Professor Kolthoff in an earlier study devoted to the voltammetry of thallium.[1] It is fitting that he contribute to this Honour Issue a paper on a related topic.

did not permit discrimination between the two alternatives.[5] However, kinetic data involving the oxidation of iron^{II} by tervalent thallium were interpreted[6] as being consistent with the formation of a bivalent thallium intermediate in accordance with the equations:

$$Fe^{2+} + Tl^{3+} \rightarrow Fe^{3+} + Tl^{II} \tag{3}$$

$$Tl^{II} + Fe^{2+} \rightarrow Fe^{3+} + Tl^{+} \tag{4}$$

The elucidation of the mechanism of the thallium^{I}-thallium^{III} electrode reaction is timely, because it has been suggested that similar transition states may be involved in electrode processes and in homogeneous electron-exchange reactions.[7] Vetter and Thiemke[8] have presented experimental evidence which is compatible with the assumption, that in 0·5–7·5 *M* aqueous sulphuric acid, reaction (1) proceeded *via* the two-step sequence:

$$Tl^{III} \overset{e}{\leftrightarrow} Tl^{II} \overset{e}{\leftrightarrow} Tl^{I} \tag{5}$$

In the investigation described in this paper, it has been shown *conclusively* that in 1*M* perchloric acid the thallium^{I}-thallium^{III} electron transfer at platinum electrodes occurred by the following mechanism:

Electroreduction of aquo-thallium^{III} ion:

$$2[Tl^{3+} + e \xrightarrow[\text{rate determining}]{k_{3,2}} Tl^{II}] \tag{6a}$$

$$2\,Tl^{II} \xrightarrow[\text{fast}]{k_{dispr}} Tl^{+} + Tl^{3+} \tag{7}$$

Electro-oxidation of aquo-thallium^{I} ion:

$$2[Tl^{+} \xrightarrow[\text{rate determining}]{k_{1,2}} Tl^{II} + e] \tag{6b}$$

$$2\,Tl^{II} \xrightarrow[\text{fast}]{k_{dispr}} Tl^{3+} + Tl^{+} \tag{7}$$

Implicit in equation (7) is direct evidence that the standard potential of the couple Tl^{II}/Tl^{+} must necessarily be more anodic than that of the Tl^{3+}/Tl^{+} couple. This accounts satisfactorily for the fact that bivalent thallium has never been prepared as a stable species in quantities amenable to chemical characterisation.

EXPERIMENTAL

The methodological approach employed for elucidating electrode kinetics was the technique of "hydrodynamic voltammetry", developed in these laboratories and previously described.[9–11] Current-voltage (c.v.) curves were recorded in a rotated electrolysis cell in which the electrolyte solution streamed past a stationary indicator electrode under judiciously controlled conditions of laminar flow.[11] The rates of the prevailing mass transport (between the bulk of the electrolyte solution and the indicator surface) corresponded within 1% to a forced convection model discussed in an earlier paper,[10] and characterised by the following equations:

$$I = \pm nFAm_i(a_i - a_i{}^0) \tag{8}$$

$$I_l = \pm nFAm_ia_i \tag{9}$$

$$m_i = \rho V^{1/2} D_i^{2/3} \nu^{-1/6} L^{-1/2} \tag{10}$$

which were verified in the present study. The symbols in equations (8)–(10) have the following meaning: I = net current (A), assigned a positive or negative sign to denote reduction or oxidation, respectively; nF = number of coulombs/mole involved in the over-all electrode reaction; I_1 = limiting current (anodic or cathodic); A = effective area of indicator electrode (cm^2); m_i = mass transport coefficient (cm/sec) for the species identified by the subscript; a_i, a_i^0 = activity (moles/ml) of species i in the bulk of the solution and at the electrode surface, respectively; ρ = a dimensionless friction drag coefficient; v = linear velocity of solution (cm/sec) past the indicator electrode; D_i = a diffusion coefficient (cm^2/sec) defined in terms of activity gradients;[12] ν = kinematic viscosity (cm^2/sec); L = characteristic dimension (cm) of electrode, parallel to flow. Concentrations of reactants and products at the indicator electrode interface (which are not accessible to direct experimental determination and are of critical importance in determining the values of the rate parameters in electrode reactions) were calculated on the basis of this mass transfer model. Two indicator electrode geometries which yielded similar results were employed, *viz.*, a conical micro electrode described previously[10] (L = the slant height of the cone) and a planar wedge electrode illustrated in Fig. 1.

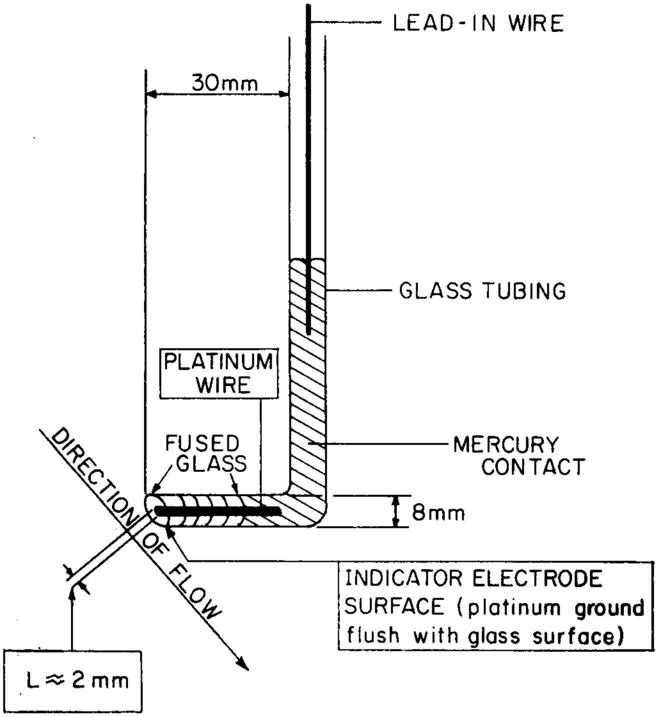

FIG. 1.—Planar wedge microelectrode
{L = characteristic dimension [see equation (10)]}

All c.v. curves were recorded in a range of potentials between 0·2 and 1·7 V versus the normal hydrogen electrode (NHE), where the platinum surface existed invariably in a reproducible "semi-oxidised" form, Pt(OH)$_n$, characterised by Feldberg.[13] As a working reference electrode, a saturated silver-silver chloride half cell (0·198 V *vs.* NHE), described by Lingane was used in conjunction with an agar gel salt bridge.[14] Appropriate precautions were taken to eliminate any consequential contamination of the electrolysis cell from the reference electrode. The electrolysis cell was constructed of polyethylene. It was ascertained, with the aid of *ad hoc* experiments carried out in all-glass apparatus, that the results obtained in this study were not affected by the polyethylene.

Voltammograms were recorded with conventional automatic polarographs, including a Sargent Model XXI instrument, and a Leeds and Northrup Electrochemograph, Model E. Potentials were scanned at rates customary in conventional polarography, *i.e.*, 1·24 to 3·33 mV/sec.

All experiments were carried out at 25·0°. Reagent-grade chemicals and triply distilled water were used. Current measurements were reproducible to within ±1%. Potential measurements were

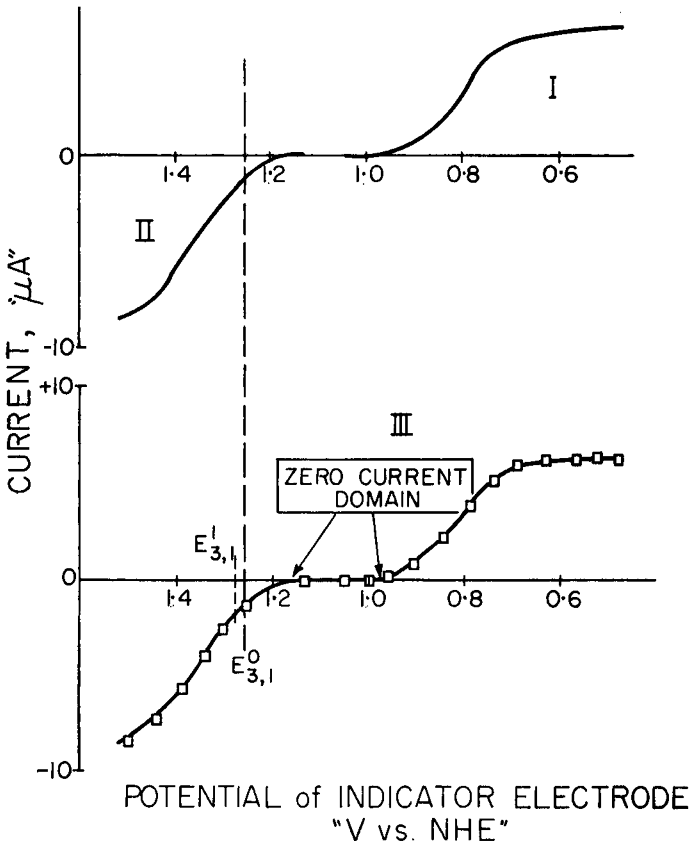

Fig. 2.—Examples of current-voltage curves obtained experimentally (flow velocity = 7·0 cm/sec): I—cathodic wave obtained in $10^{-3}M$ Tl^{3+}, in the absence of Tl^+;
II—anodic wave obtained in $10^{-3}M$ Tl^+, in the absence of Tl^{3+};
III—voltammogram obtained in mixture of $10^{-3}M$ Tl^{3+} plus $10^{-3}M$ Tl^+; smooth curve recorded experimentally; points calculated theoretically on basis of Mechanism C.
[Supporting electrolyte: $1M$ aqueous $HClO_4$; $E_3{}^0$: standard potential of Tl^{3+}/Tl^+ couple; $E_{3,1}{}'$: genuine equilibrium potential in presence of $10^{-3}M$ Tl^{3+} plus $10^{-3}M$—Tl^+ (= formal potential)]

precise and accurate to 0·005 V. Because the resistance of the electrolysis cell was 350 Ω and the maximum current measured was 50 μA, corrections for iR drops were not necessary. All potentials have been referred to the normal hydrogen electrode (NHE), using the Stockholm Sign Convention. All rate parameters reported in this paper have been consistently defined in terms of the activities of the reactants involved. This applies to the rate constants used to characterise electron transfer, as well as to mass transport coefficients [*m* in equations (8)–(10)] and diffusion coefficients. The choice of "activity rate constants", in preference to the more commonly used conventional "concentration rate constants", was predicated by considerations of fundamental consistency and general applicability (as well as convenience in correcting for electrical double layer effects, when applicable).[15]

Careful consideration was given to the magnitude of possible corrections from effects of the electric double layer.[16,17,18,19,20] At the high ionic strength used in this study ($\mu = 1$), corrections for "non-specific adsorption" proved unnecessary within the precision of the rate parameters determined (±30% for electron-transfer rate constants and ±10% for transfer coefficients). The experimental conditions were such that specific adsorption (as far as it can be assessed) was minimised.

All studies were carried out in a voltage domain which was more positive than the potential of zero charge on platinum ($\approx$0·2 V in 1*M* perchloric acid), where cations are generally not adsorbed.* The sole anion present in appreciable concentrations was perchlorate, the specific adsorption of which is known to be negligible in our working range of potentials.

RESULTS

Altogether, approximately 100 voltammograms were recorded at several concentrations and at 15 selected flow velocities in the ranges specified below:

(a) bulk concentrations of Tl^{3+}:

$5 \times 10^{-3}\,M$ to $5 \times 10^{-4}\,M$ [$3 \times 10^{-7} < a_{Tl^{3+}} < 3 \times 10^{-6}$ moles/ml]†

(b) bulk concentrations of Tl^{+}:

$5 \times 10^{-3}\,M$ to $5 \times 10^{-4}\,M$ [$3 \times 10^{-7} < a_{Tl^{+}} < 3 \times 10^{-6}$ moles/ml]†

(c) flow velocities:

5 to 90 cm/sec.

Values reported in this paper for rate parameters represent appropriately weighed averages of all of the relevant results, whose precision is indicated in terms of the standard deviation of the mean. The voltammograms illustrated in Fig. 2 are typical of the results obtained. As is evident from the figure, the cathodic wave was virtually unaffected by the presence of thallium^{I} ion and *vice versa*. Between the waves there exists a "zero current domain" (ZCD), in the potential range $1{\cdot}0 < E < 1{\cdot}2$‡. Such a situation is characteristic of "totally irreversible voltammograms",[22] indicating that at voltages corresponding to the cathodic wave, the rate of the over-all reaction

$$Tl^{+} \rightarrow Tl^{3+} + 2e \qquad (12)$$

was negligible compared to the rate of the converse process

$$Tl^{3+} + 2e \rightarrow Tl^{+} \qquad (13)$$

and *vice versa* for the anodic wave. The interesting effect of flow velocity on voltammograms is illustrated by a typical "family of curves" shown in Fig. 3.

DISCUSSION

In interpreting the experimental current voltage curves, three plausible mechanisms were considered for the electrode reaction (1);

(A) *A single stage two-electron transfer, viz.*

$$Tl^{3+} + 2e \xrightarrow{k_{3,1}} Tl^{+} \qquad (14)$$

---

* As a notable exception, Frumkin has recently reported[21] that thallium^{I} ion was adsorbed on black platinised anodes when present at a concentration of 1*M* in the bulk of the solution. The effect was appreciable at potentials between 0·3 and 0·7 V, but decreased abruptly when the voltage was made either more positive or more negative. The only potential domain where adsorption of thallium^{I} ions may have been of significance in the present study was $>1{\cdot}2$ V (*vide infra*). Extrapolation of Frumkin's data suggests that it would have been negligible in that voltage range, even under his own experimental conditions. However, in the present investigation the maximum concentration of Tl^{+} was $5 \times 10^{-3}M$ (as compared to 1*M* in reference 21) and the electrodes we used were blank (rather than black) platinum. These factors can reasonably be expected to have reduced the adsorption of thallium^{I} ion (if any) to negligible proportions. Accordingly, it was ignored.

† Concentrations were converted into corresponding activities, with the aid of applicable molarity activity coefficients, *viz.*, $f_{Tl^{3+}} = 0{\cdot}65$, $f_{Tl^{+}} = 0{\cdot}54$.

‡ Actually, the ZCD is a region where c.v. curve III had a very small slope, which coincided with the zero current axis within the precision of the present investigation.

for the cathodic wave of thallium^{III} ion; and for the anodic wave of thallium^{I} ion:

$$Tl^{+} \xrightarrow{k_{1,3}} Tl^{3+} + 2e \qquad (15)$$

(B) *Two successive one-electron transfer steps, viz.**

$$Tl^{3+} \overset{e}{\longleftrightarrow} Tl^{II} \overset{e}{\longleftrightarrow} Tl^{+} \qquad (16)$$

(C) *A rate determining one-electron transfer followed by fast disproportionation of the intermediate* in accordance with equations (6)–(7).

These three schemes are examined critically below, with a view to ascertaining whether they can account for the results obtained in this study. The applicable assumption was made that under the experimental conditions a steady state prevailed at any given potential (*i.e.*, there was no transient variation of the measured currents), and rate laws characteristic of each particular mechanism were derived accordingly.[9,22,23]

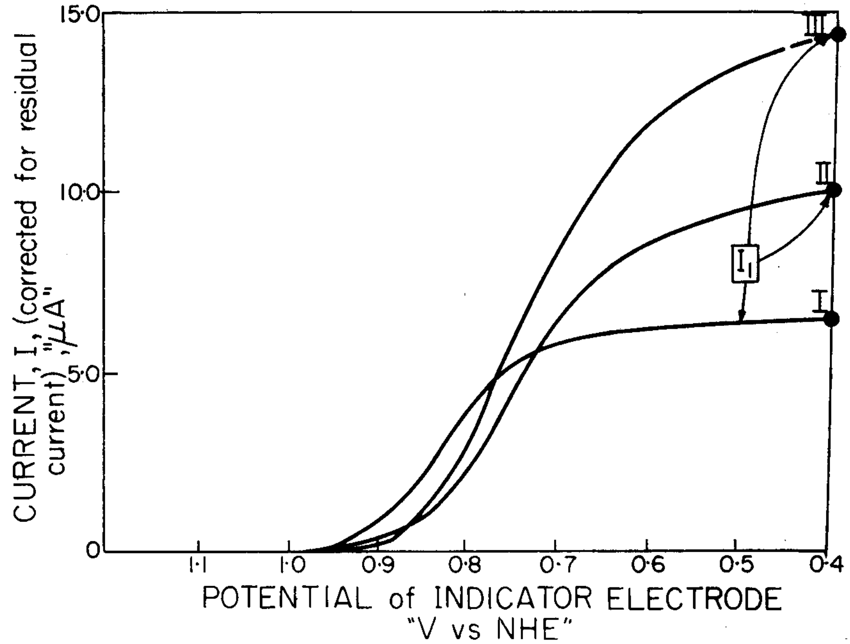

FIG. 3.—Typical "family of voltammograms" (of $10^{-3}M$ Tl^{3+} in $1M$ $HClO_4$), illustrating over-all effects of flow velocity: I—13·7 cm/sec; II—36·6 cm/sec; III—91·0 cm/sec (I_l = limiting current)

The following general observations, common to all current-voltage curves obtained, were taken into account:

(*a*) All cathodic and anodic voltammograms exhibited "shifts" as a function of flow velocity. The nature of these "shifts" is illustrated in the "normalised" voltammograms, shown in Fig. 4. These represent a replot of the data shown in Fig. 3 using as ordinate the quantity I/I_l instead of I.

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* The symbol ⟷ is used to denote a "kinetically discrete" electron-transfer step, *i.e.*, one which proceeds in the forward (reduction) or reverse (oxidation) directions via the same activated complex.

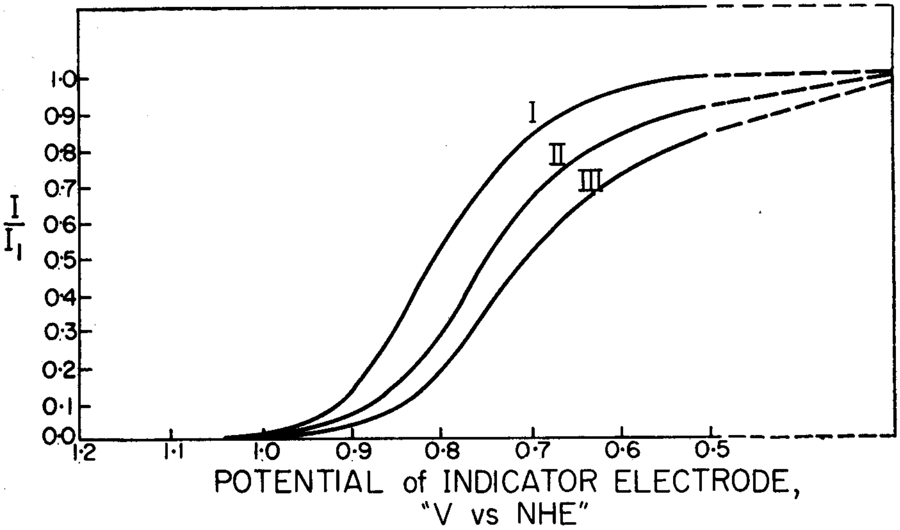

FIG. 4.—Normalised voltammograms illustrating potential shifts as function of flow velocity. Replot of data shown in Fig. 3, using the dimensionless quantity $\left(\frac{I}{I_l}\right)$ as ordinate (I = current at a given potential; I_l = limiting current)

Shifts of the type illustrated in Fig. 4 are characteristic of situations where the ascending portion of c.v. waves is controlled concomitantly by rates of electron transfer and by mass transport. Consequently, only those mechanisms were considered, in which the rate of at least one electron-transfer step is a kinetically controlling factor of the over-all reaction.

(*b*) Without exception, in all of the voltammograms recorded in this investigation, the standard potential of the thallium^{III}-thallium^{I} couple was located on the ascending part of the anodic wave, rather than in the ZCD (see Fig. 2, Curve III), *i.e.*, the apparent "overvoltage" of the cathodic wave was considerably greater than that of the anodic wave. This remarkable feature proved an important clue in the elucidation of the electrode mechanism.

Mechanism A

From the viewpoint of formal "mathematical kinetics", this is a well-known case. With respect to electron transfer, the following equations apply:

$$I = I_+ + I_- \tag{17}$$

$$I_+ = 2\,F\,A\,k_{3,1}\,a_3{}^0 \tag{18}$$

$$I_- = -2\,F\,A\,k_{1,3}\,a_1{}^0 \tag{19}$$

$$k_{3,1} = k^0{}_{3,1}\exp\left[\alpha_{3,1}(E^0_{3,1} - E)\frac{2F}{RT}\right] \tag{20}$$

$$k_{1,3} = k^0_{3,1}\exp\left[(1 - \alpha_{3,1})(E - E^0_{3,1})\frac{2F}{RT}\right] \tag{21}$$

where I_+ and I_- denote the cathodic and anodic current components; $k_{3,1}$ and $k_{1,3}$ are electron-transfer rate constants (cm/sec) effective at the potential E, for reactions (14) and (15), respectively; subscripts $_3$ and $_1$ identify activities of the thallium^{III} and thallium^{I} ions, and $E^0_{3,1}$ denotes the standard potential of the thallium^{III}-thallium^{I} couple. A crucial consideration characterising Mechanism A is that the values of the specific rate constant, $k^0_{3,1}$, and of the transfer coefficient, $\alpha_{3,1}$, must be identical irrespective of whether they are calculated form cathodic currents [equations (14) and (20)] or anodic currents [equations (15) and (21)]. *The "sameness" of these two rate parametres represents an unambiguous test as to whether only one transition state is involved, which is mandatory whenever a genuine single-stage process prevails.*

The prevailing mass transfer model requires that the following equations hold:

$$\frac{I}{2FA} = m_3(a_3 - a_3{}^0) = m_1(a_1{}^0 - a_1) \tag{22}$$

$$I_{l,+} = 2\,F\,Am_3a_3 \tag{23}$$

$$I_{l,-} = -2\,F\,Am_1a_1 \tag{24}$$

where the subscripts + and − denote cathodic and anodic limiting currents, respectively. In accordance with the steady state assumption, the *a*'s were eliminated between equations (17)–(19) and (22)–(24) yielding the following "general wave equation", which is applicable to voltammograms expected in the presence of either Tl^+ or Tl^{3+}, or both:

$$I = \frac{\dfrac{k_{3,1}}{m_3}\,I_{l,+} + \dfrac{k_{1,3}}{m_1}\,I_{l-}}{1 + \dfrac{k_{3,1}}{m_3} + \dfrac{k_{1,3}}{m_1}} \tag{25}$$

Theoretical c.v. curves, computed [from equations (20), (21) and (25)] for a solution which contains 10^{-3} *M* Tl^{3+} plus 10^{-3} *M* Tl^+, by assigning a variety of reasonable sets of values to the rate parameters $k^0_{3,1}$, α, m_3 and m_1, yielded the plots shown in Fig. 5. These represent a family of curves of a well-known type,[22] ranging in shape from

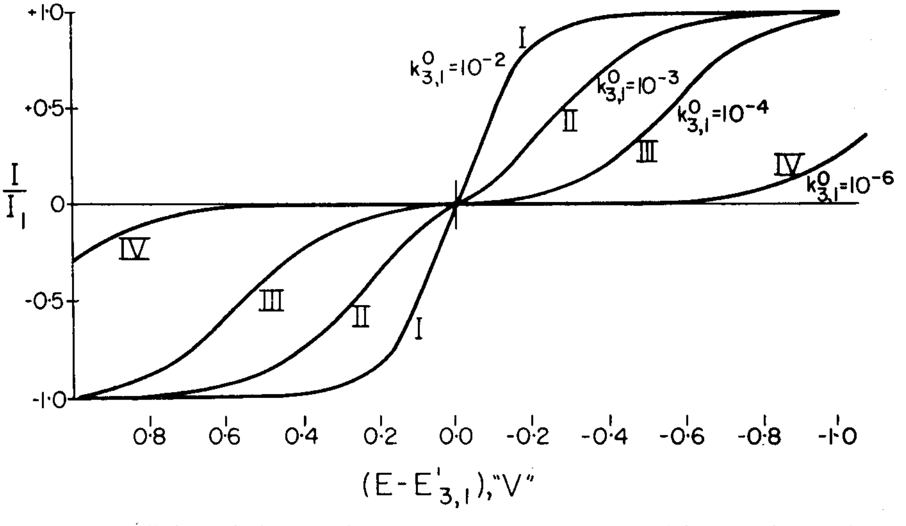

FIG. 5.—"Theoretical normalised voltammograms", calculated in accordance with Mechanism A, for a solution containing equimolar concentrations of Tl^+ plus Tl^{3+}. (E = potential of indicator electrode; $E_{3,1}{}'$ = same as in Fig. 2. Values assigned: $\alpha_{3,1} = 0{\cdot}50$; $m_3 = m_1 = 10^{-2}$ cm/sec; $k^0_{3,1}$-as shown on each curve)

a "reversible" composite wave (Curve I) via a "totally irreversible" split wave (Curve III), to Tafel plots (Curve IV). Comparisons of Fig. 5, on the one hand, with the corresponding experimental voltammogram (Fig. 2, Curve III) on the other, revealed irreconcilable differences: For instance, $E'_{3,1}$ in Fig. 5 is invariably in the ZCD, while in Fig. 2 it is located on the sigmoid section of the anodic wave. Quite generally, it was found that for all possible assignments of

$$0 < k^0_{3,1} < \infty$$

and

$$0 < \alpha^0_{3,1} < 1$$

calculations based on Mechanism A yielded c.v. curves which were significantly at variance with the experimental results.

The utter incompatibility of Mechanism A with our experimental data has been substantiated further, using the following argument. Assuming that Mechanism A did prevail, the rate parameters $k^0_{3,1}$ and $\alpha_{3,1}$ were evaluated separately from experimentally obtained cathodic and anodic c.v. waves. Using a procedure recommended in a classical paper by Laitinen *et al.*,[24] equations (18)–(21) were applied to the "foot" of the waves where concentration polarisation was negligible. This yielded two discrete sets of values, one obtained from cathodic voltammograms of Tl^{3+}, and the other from anodic voltammograms of Tl^{+}. The relevant data are listed in Table I. As can be seen in the table, the precision of the means *in each set* was better than ± 10% for $\alpha_{3,1}$ and better than ±30%, for $k^0_{3,1}$. However, the mean $k^0_{3,1}$ of the "cathodic set" differed by three orders of magnitude from that of the

TABLE I.—KINETIC PARAMETERS EVALUATED FROM THE EXPERIMENTAL DATA ON THE ASSUMPTION THAT MECHANISM A WAS OPERATIVE

Set of values obtained from cathodic waves of Tl^{3+} using equation (20)

Flow velocity, *cm/sec*	$2\alpha_{3,1}$	$k^0_{3,1}$, *cm/sec*
13·7	0·60	$1·14 \times 10^{-6}$
25·4	0·55	$1·25 \times 10^{-6}$
36·6	0·55	$0·45 \times 10^{-6}$
58·0	0·50	$1·07 \times 10^{-6}$
70·8	0·59	$1·00 \times 10^{-6}$
91·6	0·58	$0·61 \times 10^{-6}$

Averages: $\alpha_{3,1} = 0·28 \pm 0·02$; $k^0_{3,1} = (0·9 \pm 0·2) \times 10^{-6}$

Set of values obtained from anodic waves of Tl^{+} using equation (21)

Flow velocity, *cm/sec*	$2(1 - \alpha_{3,2})$	$k^0_{3,1}$, *cm/sec*
6·96	0·45	$4·8 \times 10^{-4}$
13·0	0·60	$9·0 \times 10^{-4}$
24·8	0·51	$5·8 \times 10^{-4}$
35·5	0·60	$5·8 \times 10^{-4}$
47·0	0·63	$5·9 \times 10^{-4}$
48·9	0·59	$6·3 \times 10^{-4}$
72·9	0·50	$7·1 \times 10^{-4}$
85·4	0·51	$6·3 \times 10^{-4}$
91·0	0·51	$9·1 \times 10^{-4}$

Averages: $\alpha_{3,1} = 0·72 \pm 0·03$; $k^0_{3,1} = (7 \pm 1) \times 10^{-4}$

"anodic set". The mean $\alpha_{3,1}$ values of the two sets were discrepant by a factor of three. All this indicated compellingly that more than one transition state was involved in Reaction 1.

Mechanism B

Current knowledge of the chemistry of thallium suggests strongly that the reversible standard potentials defined by equations (26) and (27) [where the subscript $_2$ identifies the bivalent thallium species in equation (16)]

$$E = E^0_{3,2} + \frac{RT}{F} \ln \frac{a_3}{a_2} \tag{26}$$

$$E = E^0_{2,1} + \frac{RT}{F} \ln \frac{a_2}{a^1} \tag{27}$$

do not differ too much (unless $E^0_{2,1} > E^0_{3,2}$, which requires a spontaneous disproportionation of bivalent thallium and leads to Mechanism C). If they did, it should have been easy to prepare bivalent thallium either by electro-oxidation of thallium^{I} ion or by the electroreduction of thallium^{III} ion. Furthermore, if

$$E^0_{2,1} \ll E^0_{3,2} \tag{28}$$

the anodic and cathodic waves shown in Fig. 2 should have each been split in two, corresponding to the appropriate discrete one-electron transfer steps. The precision and accuracy of the experiments was such that a corresponding resolution into a total of four one-electron transfer waves (in lieu of the two waves shown in Fig. 2, Curve III) would have been observed experimentally, whenever $(E^0_{3,2} - E^0_{2,1}) > 0{\cdot}05$ V.

The electron-transfer rate equations pertaining to Mechanism B are

$$I_+ = F A\, k_{3,2}\, a_3{}^0 + F A\, k_{2,1}\, a_2{}^0 \tag{29}$$

$$I_- = -F A\, k_{1,2}\, a_1{}^0 - F A\, k_{2,3}\, a_2{}^0 \tag{30}$$

Equation (31) holds concomitantly because a steady state exists

$$\frac{da_2}{dt} = 0 \rightarrow k_{3,2}\, a_3{}^0 + k_{1,2}\, a_1{}^0 = k_{2,3}\, a_2{}^0 + k_{2,1}\, a_2{}^0 \tag{31}$$

Relevant rate constants, transfer coefficients and potentials are correlated as follows:

$$k_{3,2} = k^0_{3,2} \exp\left[\alpha_{3,2}(E^0_{3,2} - E)\frac{F}{RT}\right] \tag{32}$$

$$k_{2,3} = k^0_{3,2} \exp\left[(1 - \alpha_{3,2})(E - E^0_{3,2})\frac{F}{RT}\right] \tag{33}$$

$$k_{2,1} = k^0_{2,1} \exp\left[\alpha_{2,1}(E^0_{2,1} - E)\frac{F}{RT}\right] \tag{34}$$

$$k_{1,2} = k^0_{2,1} \exp\left[(1 - \alpha_{2,1})(E - E^0_{2,1})\frac{F}{RT}\right] \tag{35}$$

$$E^0_{3,1} = \frac{E^0_{3,2} + E^0_{2,1}}{2} \tag{36}$$

Elimination of all activity terms between equations (22)–(24) and (29)–(31) yielded the "general wave equation":

$$I \doteq \frac{\dfrac{k_{3,2}\,k_{2,1}}{m_3}\,I_{1,+} + \dfrac{k_{1,2}\,k_{2,3}}{m_1}\,I_{1,-}}{k_{2,3} + k_{2,1} + \dfrac{k_{3,2}\,k_{2,1}}{m_3} + \dfrac{k_{1,2}\,k_{2,3}}{m_1}} \qquad (37)$$

Theoretical voltammograms corresponding to equations (32)–(35) and (37) were constructed with the aid of calculations similar to those employed in obtaining Fig. 5. Judicious comparison with experimental c.v. curves indicated unambiguously that Mechanism B could not account satisfactorily for the experimental observations, regardless of the values assigned to the rate parameters $k^0_{3,2}$, $k^0_{2,1}$, $\alpha_{3,2}$ and $\alpha_{2,1}$. That Mechanism B was indeed not operative is evident from the fact that in an equimolar solution of Tl^{3+} and Tl^{+}, where

$$\frac{a_3}{f_3} = \frac{a_1}{f_1} \qquad (38)$$

equation (37) requires that

$$I = 0 \; at \; E = E'_{1,3} = E^0_{1,3} + \frac{RT}{2F} \ln \frac{f_3}{f_1} \qquad (39)$$

Mathematical proof, that requirement (39) is mandatory for Mechanism B whenever Tl^{3+} plus Tl^{+} are present in equimolar bulk concentrations, is offered in the *Appendix*. It can be seen in Fig. 2, Curve III (which is a typical example of a voltammogram actually recorded in an equimolar solution of Tl^{3+} plus Tl^{+}) that the results obtained in this investigation were strikingly at variance with requirement (39). Consequently, Mechanism B has been ruled out.

Mechanism C

In accordance with equations (6)–(7) the following rate laws apply:

$$I_+ = 2\,F A\,k_{3,2}\,a_3{}^0 \qquad (40)$$

$$I_- = -2\,F A\,k_{1,2}\,a_1{}^0 \qquad (41)$$

Concomitantly, rate and potential parameters must conform with equations (32)–(36), mass transport is governed by equations (22)–(24), and the following Steady State Requirement [based on equations (7), (40), (41)] must be met:

$$\frac{da_2{}^0}{dt} = 0; \quad k_{3,2}\,a_3{}^0 + k_{1,2}\,a_1{}^0 = \delta k_{\text{dispr.}}\,(a_2{}^0)^2 \qquad (42)$$

where δ denotes the thickness of the reaction layer at the electrode surface. The corresponding general wave equation (obtained by appropriate elimination of the activity terms) has the form:

$$I = \frac{\dfrac{k_{3,2}}{m_3}\,I_{1,+} + \dfrac{k_{1,2}}{m_1}\,I_{1,-}}{1 + \dfrac{k_{3,2}}{m_3} + \dfrac{k_{1,2}}{m_1}} \qquad (43)$$

Theoretical voltammograms computed in accordance with equation (43) gave plots which proved, in all instances, identical with the corresponding experimental c.v.

curves. The excellent agreement is exemplified by the "calculated points", superimposed on Fig. 2, Curve III.

Numerical estimates of rate parameters, calculated from experimental voltammograms on the basis of equation (43) are listed in Table II

TABLE II—KINETIC PARAMETERS CALCULATED FROM THE EXPERIMENTAL DATA ON THE ASSUMPTION THAT MECHANISM C WAS OPERATIVE

Set of values obtained from cathodic waves of Tl^{3+} using equations (40) and (43)

Flow velocity, *cm/sec*	$\alpha_{3,2}$	$k_{3,2}$ (at 1·25 V)[a]
13·7	0·60	$1{\cdot}14 \times 10^{-6}$
25·4	0·55	$1{\cdot}25 \times 10^{-6}$
36·6	0·55	$0{\cdot}45 \times 10^{-6}$
58·0	0·50	$1{\cdot}07 \times 10^{-6}$
70·8	0·59	$1{\cdot}00 \times 10^{-6}$
91·8	0·58	$0{\cdot}61 \times 10^{-6}$

Average: $\alpha_{3,2} = 0{\cdot}56 \pm 0{\cdot}03$; $k_{3,2} = (0{\cdot}9 \pm 0{\cdot}2) \times 10^{-6}$

Set of values obtained from anodic waves of Tl^{+} using equations (41) and (43)

Flow velocity *cm/sec*	$(1 - \alpha_{2,1})$	$k_{1,2}$ (at 1·25 V)[a]
6·97	0·45	$4{\cdot}8 \times 10^{-4}$
13·0	0·60	$9{\cdot}0 \times 10^{-4}$
24·8	0·51	$5{\cdot}8 \times 10^{-4}$
35·5	0·60	$5{\cdot}8 \times 10^{-4}$
47·0	0·63	$5{\cdot}9 \times 10^{-4}$
48·9	0·59	$6{\cdot}3 \times 10^{-4}$
72·9	0·50	$7{\cdot}1 \times 10^{-4}$
85·4	0·51	$6{\cdot}3 \times 10^{-4}$
91·0	0·51	$9{\cdot}1 \times 10^{-4}$

Average: $\alpha_{2,1} = 0{\cdot}45 \pm 0{\cdot}05$; $k_{1,2} = (7 \pm 1) \times 10^{-4}$

[a] Because $E^0_{3,2}$ and $E^0_{2,1}$ are not known, values of $k_{3,2}$ and $k_{2,1}$ effective at $E^0_{3,1}$ (= 1·25 V) have been reported.

It is apparent that the values obtained at fifteen different flow velocities exhibited satisfactory "internal consistency" and the transfer coefficients $\alpha_{3,2}$ and $\alpha_{2,1}$ approximate 0·5 in agreement with reasonable *a priori* considerations. This confirms that under the experimental conditions prevailing in this investigation, the thallium^{I}-thallium^{III} electron transfer occurred via Mechanism C [equations (6)–(7)].

The finding, that in 1 *M* perchloric acid the thallium^{I}-thallium^{III} reaction involves a fast disproportionation of the bivalent intermediate, invites an interesting comparison with the report of Vetter and Thiemke.[8] In the presence of sulphuric acid in appreciable concentration, the same process was compatible with Mechanism B. It is noted in this context, that Vetter and Thiemke's experimental results are also compatible with Mechanism C. In other words, their data did not permit discrimination between Mechanisms B and C. The possibility, that the shape of d.c. voltammograms may be sometimes inconclusive for the purpose of identifying mechanisms of electrode processes, has been pointed out by Riddiford.[25] The experimental situation in the present investigation was fortunate in this respect. The genuine equilibrium potential of the thallium^{I}-thallium^{III} couple ($E'_{3,1}$ in the presence of equimolar concentrations of Tl^{+} plus Tl^{3+}) was invariably located *outside the ZCD* (see Fig. 2). This has permitted us to select *Mechanism C* as *uniquely applicable*, without ambiguity. However, we desire to emphasise that there is no necessary contradiction between Vetter and Thiemke's conclusions and ours. Quite possibly, the rates and mechanism of the thallium^{I}-thallium^{III} electrode reaction may be entirely different in perchloric and in sulphuric acids. Appreciable sulphato-complexation of thallium^{I} and thallium^{III} ion is known to occur in sulphate media.[8,26] Consequently, the electroreactive species are not necessarily the same in the presence of sulphate as in perchloric acid (where the aquo ions prevail). Furthermore, the presence of sulphate and/or perchlorate may quite radically change the rates and the mechanism if, for instance, a "bridged" transition state were involved. It should be noted, in this context, that Mechanism C may readily be converted into B if the rate of disproportionation [equation (7)] is slow compared to the rate of the electron-transfer steps (6a) and (6b). This is evident from the following scheme.

$$\begin{tikzcd}[column sep=large] \text{PATH I:}\ \mathrm{Tl}^{3+} \arrow[r, leftrightarrow, "e"] & \mathrm{Tl}^{II} \arrow[r, leftrightarrow, "e"] \arrow[l, bend left, "\substack{\text{PATH IIa}\\ \text{Oxidation of Tl}^{II}}"] \arrow[r, bend right, "\substack{\text{PATH IIb}\\ \text{Reduction of Tl}^{II}}"'] & \mathrm{Tl}^{+} \end{tikzcd} \tag{44}$$

If the rate of reaction (7) is slow compared to the electron-transfer processes

$$\mathrm{Tl}^{II} \overset{e}{\longleftrightarrow} \mathrm{Tl}^{+} \tag{45}$$

$$\mathrm{Tl}^{II} \overset{e}{\longleftrightarrow} \mathrm{Tl}^{3+} \tag{46}$$

the over-all electrode reaction [equation (1)] must proceed via "PATH I" (as may have been the case in Vetter and Thiemke's work). Alternative PATH II would be operative (as was the case in the present investigation) in the following situations

$$r_7 \gg r_{45} \tag{47}$$

$$r_7 \gg r_{46} \tag{48}$$

where the symbol *r* denotes the rate of the reaction identified by the subscripts (which are identical with the serial numbers of the corresponding chemical equations listed earlier in this article).

The possibility of a mechanism where $r_7 \approx r_{45} \approx r_{46}$ was rejected, on the grounds that it would be characterised by a gradual changeover from Mechanism C to Mechanism B as a function of the concentration of the "primary reactants" Tl^{3+} and Tl^{+}: reaction (7) is second order with respect to Tl^{II}, while reactions (45) and (46) both have first order kinetics. Consequently, Mechanism B would be expected to predominate at low concentrations of Tl^{+} and Tl^{3+}, and Mechanism C at high concentrations. No such trend was evident in the present investigation.

In conclusion, it is apparent that the thallium^{III}-thallium^{I} electrode reaction proceeds via a bivalent intermediate which is a stronger oxidant than Tl^{3+}. In aqueous solution, and in the absence of complexing ligands, the relevant redox potentials [identified in expression (49)]

$$\begin{tikzcd}[column sep=large] \mathrm{Tl}^{3+} \arrow[r, leftrightarrow, "E^0_{3,2}"] \arrow[rr, leftrightarrow, bend right, "E^0_{3,1}"'] & \mathrm{Tl}^{II} \arrow[r, leftrightarrow, "E^0_{2,1}"] & \mathrm{Tl}^{+} \end{tikzcd} \tag{49}$$

are characterised by the following relative properties:

$$E^0_{2,1} > E^0_{3,1} \tag{50}$$

$$2E^0_{3,1} = E^0_{3,2} + E^0_{2,1} \tag{51}$$

Disproportionation of bivalent thallium into Tl^{3+} plus Tl^{+}, as required by relation (50), occurred in the presence of perchloric acid at a rate which was fast compared to reactions (45) and (46).

APPENDIX

Proof of requirement (39)

Because the denominator of equation (37) is finite, the necessary and sufficient condition for

$$I = 0 \tag{A1}$$

is that the numerator be equal to zero, *viz.*:

$$\frac{k_{3,2} \,.\, k_{2,1}}{m_3} I_{1,+} + \frac{k_{1,2} \,.\, k_{2,3}}{m_1} I_{1,-} = 0 \tag{A2}$$

Substituting for *k* the appropriate potential dependent expressions [equations (32)–(35)] and rearranging equation (A2), yielded:

$$\exp\left\{[2E - (E^0_{3,2} + E^0_{2,1})]\frac{F}{RT}\right\} = -\frac{m_1 I_{1,+}}{m_3 I_{1,-}} \tag{A3}$$

Expressing $(E^0_{3,2} + E^0_{2,1})$ and the quotient on the right side in terms of equivalent quantities via equations (36), (23) and (24), equation (A4) was obtained.

$$\exp\left\{(E - E^0_{3,1})\frac{2F}{RT}\right\} = \frac{a_3}{a_1} \tag{A4}$$

Applying equation (38) and taking logarithms, equation (39) was readily obtained:

$$(38) \rightarrow \frac{a_3}{a_1} = \frac{f_3}{f_1}\,; \qquad (A4) \rightarrow E_{I=0}\, E^0_{3,1} + \frac{RT}{nF} \ln \frac{f_3}{f_1}$$

Acknowledgments—The authors wish to acknowledge gratefully the suggestions of Professor R. A. Marcus (Polytechnic Institute of Brooklyn).*

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Zusammenfassung—Die Thallium(I)- Thallium(III)- Elektrodenreaktion wurde mit Hilfe der hydrodynamischen Voltammetrie an Platinanoden und -kathoden untersucht. Es werden schlüssige Beweise dafür angegeben, dass die Elektrooxydation des hydratisierten Tl^{+} und die Elektroreduktion von Tl^{3+} über eine zweiwertige Thalliumstufe verlaufen. Tl(II) ist ein stärkeres Oxydationsmittel als Tl(III). In 1m wässriger Überchlorsäure war die Geschwindigkeit der Disproportionierung

$$2\,Tl(II) \rightarrow Tl^{+} + Tl^{3+}$$

schnell im Vergleich den Elektronenübergängen

$$Tl(II) + e \rightarrow Tl^{+}$$

und $$Tl^{3+} + e \rightarrow Tl(II).$$

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* Preliminary assignments of values for two-electron transfer rate constants were made available to Dr. Marcus while the investigation described in this paper was still in progress. They have been incorporated for documentation purposes in a recent theoretical paper[7] and identified as "unpublished results". The values given in the present article are considered definitive assignment, superseding the preliminary data reported by Marcus.

This investigation was supported in part by Public Health Service Research Grant HE-02342 from the National Heart Institute.

Résumé—La réaction Tl^{3+}/Tl^{+} aux électrodes a été étudiée par voltampérométrie hydrodynamique sur cathodes et anodes de platine. On montre que l'électrooxydation de l'ion Tl^{+} en milieu aqueux et l'électroréduction de Tl^{3+} font intervenir une forme divalente du thallium. Tl(II) est un oxydant plus fort que l'ion thallique. Dans l'acide perchlorique 1 M la vitesse de la réaction de dismutation

$$2\,Tl(II) \rightarrow Tl^{+} + Tl^{3+}$$

est relativement rapide comparée aux étapes du transfert électronique:

$$Tl(II) + e \rightarrow Tl^{+}$$

$$Tl^{3+} + e \rightarrow Tl(II)$$

REFERENCES

[1] I. M. Kolthoff and J. Jordan, *J. Amer. Chem. Soc.*, 1952, **74**, 382.
[2] J. Weiss, *Nature*, 1934, **133**, 648.
[3] N. Uri., *Chem. Rev.*, 1951, **50**, 375.
[4] R. Stewart, *Experientia*, 1959, **15**, 401.
[5] R. Roig, and R. W. Dodson, *J. Phys. Chem.*, 1961, **65**, 2175.
[6] K. G. Ashurt and W. C. Higginson, *J. Chem. Soc.*, 1953, 3044.
[7] R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853.
[8] K. J. Vetter and G. Thiemke, *Z. Electrochem.*, 1960, **64**, 805.
[9] J. Jordan, and R. A. Javick, *Electrochim. Acta*, 1962, **6**, 23.
[10] J. Jordan, R. A. Javick, and W. E. Ranz, *J. Amer. Chem. Soc.*, 1958, **80**, 3846.
[11] J. Jordan, *Analyt. Chem.*, 1955, **27**, 1708.
[12] J. Jordan, L. Ackerman and R. L. Berger, *J. Amer. Chem. Soc.*, 1956, **78**, 2979; J. Jordan and W. E. Bauer, *ibid.*, 1959, **81**, 3915.
[13] S. W. Feldberg, Ph. D. Thesis, Princeton, 1961.
[14] J. J. Lingane, *Electroanalytical Chemistry.* Interscience, New York, 2nd Ed., 1958, pp. 363–364.
[15] H. A. Catherino, Ph. D. Thesis, Pennsylvania State University., 1963.
[16] P. Delahay, *Progress in Polarography*, P. Zuman Ed., Vol. I. Interscience Publishers, New York 1962, pp. 65–80.
[17] C. N. Reilley and W. Stumm, *Progress in Polarography*, P. Zuman, Ed., Vol. I. Interscience Publishers, New York, 1962 pp. 81–121.
[18] R. Parsons, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. I., P. Delahay, Ed. Interscience Publishers, New York, 1961, pp. 1–64.
[19] A. N. Frumkin, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. I., P. Delahay, Ed. Interscience Publishers, New York, 1961, pp. 65–121.
[20] A. N. Frumkin and N. Nikolaeva-Fedorovich, *Progress in Polarography*, P. Zuman, Ed., Vol. I. Interscience Publishers, New York, 1962, pp. 223–241.
[21] A. Frumkin, *Electrochim. Acta*, 1961, **5**, 265.
[22] P. Delahay, *New Instrumental Methods in Electrochemistry.* Interscience Publishers, New York, 1954.
[23] J. Jordan and N. R. Stalica, *Handbook of Analytical Chemistry*, L. Meites, Ed. McGraw-Hill, New York, 1963, Section 5, pp. 38–46.
[24] P. Kivalo, K. B. Oldham and H. A. Laitinen, *J. Amer. Chem. Soc.*, 1953, **75**, 4148.
[25] A. C. Riddiford, *J. Chem. Soc.*, 1960, 1175.
[26] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, *Stability Constants*, Special Publications No. 7, Part II. The Chemical Society, London, 1958, p. 85.

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POLAROGRAPHIC DETERMINATION OF CERTAIN MEDICINAL COMPOUNDS CONTAINING DICHLORACETAMIDO GROUPS*

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Summary—A polarographic study has been made of a variety of compounds containing dichloracetamido groups, including *N*-(2,4-dichlorobenzyl)-*N*-(2-hydroxyethyl)dichloracetamide (chlorbetamide), *N*-(4-methylsulphonylphenyl)-1,3-dihydroxy-2-propyldichloracetamide (racephenidol), *N*,*N'*-bis-(2-ethoxyethyl)-*N*,*N'*-*p*-xylylene-bis-dichloracetamide (teclozan), *N*,*N'*-octamethylene-bis-dichloracetamide and their corresponding analogues. Analytical results are discussed from a quantitative and qualitative point of view with special emphasis on the stability of the compounds at various pH and the effect of various elements or groups in the molecule on the half-wave potentials of the two resulting cathodic waves.

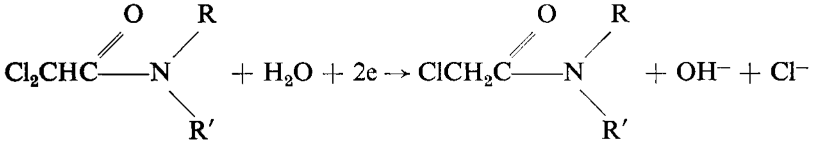
INTRODUCTION

IN the past, little attention has been given polarographically to the dichloracetamido group in medicinal compounds. Chloramphenicol, D(−)-threo-2,2-dichloro-*N*-[*β*-hydroxy-*α*-(hydroxymethyl)-*p*-nitrophenethyl]-acetamide, has been studied polarographically by Hess[1], Varela,[2] and Knobloch and Svatek.[3] The emphasis was, however, on the reduction characteristics of the nitro group rather than the dichloracetamido group. Elving and Ching-Siang Tang[4,5,6] have shown the polarographic characteristics of mono-, di- and trichloracetic acid as well as esters of these acids. In many respects the compounds described in the present paper are like the esters of dichloracetic acid in that as long as they remain intact two cathodic waves result when polarographed.

If the compounds are split by hydrolysis, only one cathodic wave develops, showing all of the polarographic characteristics of dichloracetic acid. These compounds, being amides, are not as susceptible to hydrolysis as are the esters of dichloracetic acid.

The mechanism for these polarographic reductions, representing the successive removal of chlorine from the dichloracetyl portion of the molecule, would be the same as Elving has stated and for the same reasons:—

First Cathodic Wave:



$$Cl_2CHC(=O)-N(R)(R') + H_2O + 2e \rightarrow ClCH_2C(=O)-N(R)(R') + OH^- + Cl^-$$

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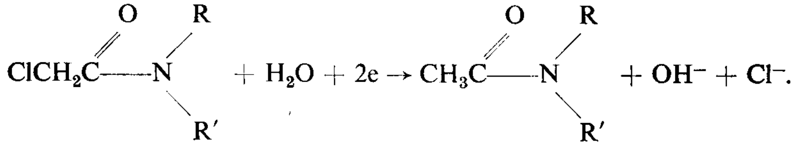
† Fellow of the American Foundation for Pharmaceutical Education.

Second Cathodic Wave:



$$\mathrm{ClCH_2C(=O)N(R)R'} + \mathrm{H_2O} + 2e \rightarrow \mathrm{CH_3C(=O)N(R)R'} + \mathrm{OH^-} + \mathrm{Cl^-}.$$

It is the purpose of this communication to show the polarographic characteristics of a variety of compounds containing the dichloracetamido group. The compounds have been divided into four major groups (Table I).

EXPERIMENTAL

Reagents

All chemicals and organic solvents were reagent grade. Nitrogen was Edison's dry high-purity nitrogen. Distilled water was used throughout as a solvent as well as in rinsing the polarographic cell.

The buffers were constant ionic strength (1*M*) McIlvaine pH 3, 4, 5, 6, 7 and 8 buffers[7] and a 2·5*M* constant ionic strength aqueous ammonia–ammonium chloride buffer pH 8·2. Unless otherwise stated, the ionic strength of the polarographic media was 0·5*M*. The buffers were adjusted to the stated pH ± 0·1. On addition of these buffers to the polarographic medium the pH of the resulting medium was changed:

in 10% methanol the pH was 0·2–0·3 unit higher;
in 50% methanol the pH was nearly 1 unit higher;
in 70% methanol–10% *N,N*-dimethylformamide (DMF) the pH was 0·5–0·6 unit lower.

Because the polarographic waves resulting from the dichloracetamido groups are independent of pH in the pH range studied, the pH mentioned in the text will refer to that of the aqueous buffer.

Sample solutions: Stock solutions of Group I, II and IV compounds (0·005, 0·005 and 0·0025*M*, respectively) were prepared in 50 ml of methanol. Because of their poor solubility in methanol, 0·0025*M* solutions of the compounds of Group III were prepared in 50 ml of DMF.

Apparatus

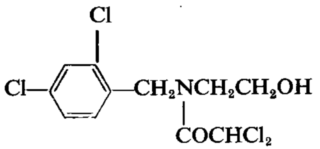
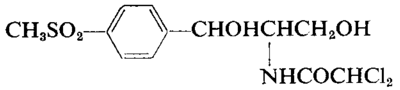
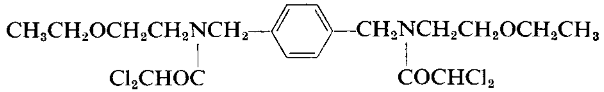
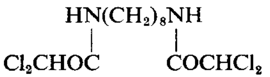
A Sargent Recording Polarograph Model XXI with a conventional dropping mercury electrode (DME) and an aqueous saturated calomel electrode (SCE) were used throughout these studies at a sensitivity setting of 0·06 μA/mm of scale. The damping switch was set at number one. The polarographic cell was a Lingane and Laitinen H-type cell with an agar potassium chloride salt bridge. Unless otherwise stated, all polarograms were recorded in a Sargent constant temperature bath set at 25·0 ± 0·1°. The capillary used in these studies had the following characteristics in 0·5*M* pH 8 McIlvaine buffer in 50% methanol (open circuit): m = 1·861 mg/sec and t = 4·28 sec for h = 50 cm.

All polarograms were recorded with the mercury height (h) at 50 cm. All diffusion currents were corrected for residual current, which never exceeded 0·2 μA for any potential at which the diffusion current was measured. Maxima were occasionally observed with the second wave but never the first. No maximum suppressors, which might distort the resulting waves, were added to any of the solutions. The half-wave potentials reported are not corrected for iR drop (cell resistance). A Beckman pH meter, Model G, was used to measure pH of the various buffers and solutions.

General procedure for recording the current-voltage curves

Five ml (by pipette) of the appropriate stock solution were added to a 50-ml volumetric flask containing the desired buffer and methanol concentration. For Groups I, II and IV the medium consisted of 25 ml of the 1*M* buffer and 20 ml of methanol. For Group III the medium consisted of 10 ml of 2·5*M* aqueous ammonia–ammonium chloride buffer pH 8·2 and 35 ml of methanol. In each case the solvent mixture was allowed to cool to room temperature before addition of the sample. After the sample addition, the solution was diluted to volume with water and mixed. About 20 ml of this buffered solution was then polarographed within 15 min and the remaining portion after standing 3 days at room temperature. Nitrogen was first passed through a wash bottle containing the same solvent and buffer as the sample, then through the polarographic cell containing the sample for 5 min to deaerate the medium. During the recording of the polarogram (0·0 to −2·0 V) nitrogen was passed over the surface of the solution but without disturbing it. From the resulting polarograms, the half-wave potentials were determined by the intersecting point method[8] and the diffusion current was determined by subtracting the extrapolated residual current from the extrapolated limiting

TABLE I

Group	Structure and chemical name of representative medicinal compound	Generic name	Major medicinal activity
I	 *N*-(2,4-dichlorobenzyl)-*N*-(2-hydroxyethyl) dichloracetamide	Chlorbetamide	Amebicidal
II	 *N*-(4-methylsulphonylphenyl)-1,3-dihydroxy-2-propyldichloracetamide	Raceophenidol	Antibacterial
III	 *N*,*N*′-bis(2-ethoxyethyl)-*N*,*N*′-*p*-xylylene-bis-dichloracetamide	Teclozan	Amebicidal
IV	 $\underset{Cl_2CHOC}{\vert}\text{HN}(CH_2)_8\text{NH}\underset{COCHCl_2}{\vert}$ *N*,*N*′-octamethylene-bis-dichloracetamide	None	Antispermatogenic

current at the half-wave potential of the first wave. The diffusion current of the second wave was determined by subtracting the extrapolated limiting current of the first wave from the extrapolated limiting current of the second wave. Using this approach a satisfactory method was applicable. on a comparative basis, to all of the waves obtained. The diffusion current constant (I) was calculated from data obtained from these polarograms: $I = i_d/Cm^{2/3}t^{1/6}$ where i_d is expressed in μA, C in mmoles (of the given compound)/litre, m in mg (of mercury)/sec and t in sec (length of time for 1 drop of mercury at the stated potential at which the diffusion current was measured).

RESULTS AND DISCUSSION

General

The polarographic waves of these dichloracetamido compounds are well-defined irreversible waves, in that they do not comply with the accepted criteria for reversibility. The change in slope for both waves is gradual and usually over a 0·3-V span. The half-wave potentials vary with concentration (become more negative with increasing concentration). The average diffusion current constant (I) values are in good agreement, as shown in Table II. The I values for the bisdichloracetamido compounds (Groups III and IV) are about twice the values of the mono-dichloracetamido compounds (Groups I and II). This is added evidence that the resulting polarographic waves are from the amount of the dichloracetamido in the given compound. Even though the second wave is not as well-defined as the first, its average I value is in close agreement with that of the first wave. This again is evidence for the reduction of the chlorines individually, from the dichloracetamido group.

TABLE II

$$I^* = \frac{i_d}{Cm^{2/3}t^{1/6}}$$

Group	Average I-Value for first wave	Average I-Value for second wave
I	1·55	1·72
II	1·49	1·42
III	2·92	3·32
IV	2·90	3·01

* I is the diffusion current constant where i_d is expressed in μA, C in mmoles/litre, m in mg/sec and t in sec.

The temperature coefficient for these dichloracetamido compounds is 1·5 to 2·0% between 20° and 40°. On changing the mercury column height from 30 to 90 cm, the ratio of $i/h^{1/2}$ was found to be constant. The current resulting from the reduction of these chlorine atoms is diffusion controlled current (i_d) according to the existing criteria.

With none of the compounds did pH (in the pH 3–8 range) affect the wave-height or the half-wave potential of the freshly prepared solution of a given compound.

The ionic strength of the media was varied from 0·1 to 0·5*M* without affecting any of the polarographic wave characteristics of the compounds. The methanol content in the polarographic media was varied from 10 to 80%. With most of the compounds, the current decreases about 20% when the methanol content is increased from 10 to 50%. The half-wave potentials usually become more negative (of the order of 0·03 to 0·3 V) as the methanol content increased from 10 to 50%.

With the Group I and II compounds, the diffusion current (corrected for residual current) for the first wave is proportional to concentration from 0·0002 to 0·001*M* (the highest concentration tested). For the bis-dichloracetamido compounds (Groups III and IV) the range is 0·0001 to 0·001*M*.

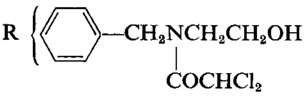
When related compounds were available, containing the several amido groupings (acetyl, mono-, di- or trichloracetyl), it was found that the polarographic waves are very closely related. With the trichloracetamido group, three polarographic waves result. The first appearing to be nearly reversible with a half-wave potential between 0·1 and 0·2 V. The second wave has the same half-wave potential as the first wave of the dichloracetamido group. The third wave has the same half-wave potential as the second wave of the dichloracetamido group and the same as the single wave of the monochloracetamido group. The simple acetamido group results in no wave other than that of the residual current. With the various waves the diffusion current constants are quite similar.

When polarographed, all of the compounds containing the dichloracetamido group resulted in two cathodic waves which are well suited for both the qualitative and quantitative analysis of the intact compounds as well as the main hydrolysis product, the dichloracetate ion. It is from this approach that the compounds will be discussed under their respective groupings.

Group I

Effect of ring substituents. The positioning of the halogen atoms on the benzyl nucleus (Table III) alters the half-wave potential of the first reduction wave of this group of compounds. The 3,4-dichloro analogue's half-wave potential is nearly 0·2 V more positive (thus making the first chlorine of the dichloraceto group easier to reduce) than the 2,6-dichloro analogue. Between these extremes the half-wave potentials of the other halogen compounds are found.

TABLE III.—POLAROGRAPHIC REDUCTION OF GROUP I COMPOUNDS IN BUFFERED 50% METHANOL



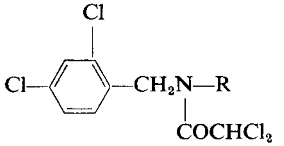
R	First wave		Second wave		Hydrolysed after 3 days at pH 8, %
	$-E_{1/2}$	I	$-E_{1/2}$	I	
1 3,4-dichloro	0·46	1·38	1·20	1·41	72
2 2,4-dibromo	0·49	1·29	1·12	1·57	42
3 4-chloro	0·50	1·38	1·19	1·40	47
4 2,4-dichloro	0·51	1·58	1·16	1·88	64
5 2,6-dichloro	0·63	1·34	1·28	1·26	54
6 4-C_2H_5O—	0·51	1·07	1·18	1·27	82
7 4-C_4H_9O—	0·54	1·13	1·18	1·44	83
8 3,4-diCH_3O—	0·55	1·21	1·18	1·52	76
9 3,4-CH_2O_2—	0·55	1·34	1·20	1·50	89

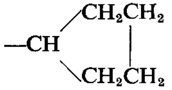
The presence of various alkoxy groups on the benzyl nucleus (Table III) does not appreciably change the polarographic characteristics of the dichloracetamido group.

Effect of substituents on the amide nitrogen. The changes in half-wave potentials of the dichloracetamido group resulting from the various groups on the tertiary amide are not extreme, as shown in Table IV.

From the values (Hydrolysis, %) in the last column of Tables III and IV, the effect of the adjacent substituents on the hydrolysis of the dichloracetamido group is

TABLE IV.—POLAROGRAPHIC REDUCTION OF GROUP I COMPOUNDS IN BUFFERED 50% METHANOL



	R	First Wave		Second Wave		Hydrolysed after 3 days at pH 8, %
		$-E_{1/2}$	I	$-E_{1/2}$	I	
10	$—CH_2CH_2CH_2OH$	0·46	1·62	1·15	1·87	None
11	$—CH_2CHOHCH_3$	0·47	1·78	1·15	1·88	None
12	$—CH_2CH_2OH$*	0·51	1·58	1·16	1·88	64
13	$—CH_2CH_2OCH_3$	0·49	1·76	1·13	2·08	None
14	$—CH_2CH_2OC_2H_5$	0·51	1·63	1·14	1·84	None
15	$—CH_2CH_2OCOCH_3$	0·41	1·90	1·10	2·18	60
16	$—CH_2CH_2OCOCH_2CH_2Cl$	0·42	1·66	1·11	1·72	56
17	$—CH_2CH_2CN$	0·37	1·90	1·07	2·05	None
18	$—CH_2CH_2CONH_2$	0·45	1·77	1·16	1·80	None
19	$—CH_3$	0·50	1·80	1·14	2·07	None
20	$—CH(CH_3)_2$	0·49	1·70	1·16	1·69	None
21		0·51	1·84	1·11	1·97	None

* This is the same compound as number 4 in Table III.

quite apparent. Only the compounds which contain the 2-hydroxyethyl group (numbers 1–9) or the 2-acyloxyethyl group (numbers 15 and 16) attached to the amide nitrogen show any tendency towards hydrolysis of the dichloracetamido group in the 50% methanol pH 8 medium at room temperature. This hydrolysis of the dichloracetamido group may be followed polarographically through the reduction waves of the chlorine on the dichloracetyl group. As long as the dichloracetyl group is still attached to the nitrogen, the two resulting waves are those characteristic of the individual chlorines from the dichloracetamido group being reduced. When about 10% of the dichloracetamido group is hydrolysed, a third wave is detected in the polarogram. The wave height of this third wave increases as the hydrolysis of the dichloracetamido group proceeds to completion. When the dichloracetamido group is 100% hydrolysed, only one reduction wave remains which has all of the polarographic characteristics of dichloracetic acid in this same medium.

With the various compounds containing the 2-hydroxyethyl group there is no apparent correlation between the rate of hydrolysis of the dichloracetamido group and the ease of reduction polarographically of the first chlorine of the dichloracetamido group. It is noted, however, that the amount of hydrolysis taking place in this pH 8 medium at room temperature in 3 days depends on the R-substituent of the molecule. The alkalinity of the medium also plays an important role on the rate of hydrolysis of the dichloracetamido group: if the pH 8 buffer is replaced with 0·1*M* tetramethylammonium hydroxide, the dichloracetamido group of chlorbetamide is 100% hydrolysed within 15 min at room temperature, whereas in the pH 8 buffer only 64% is hydrolysed after 3 days at room temperature. In an acidic medium (pH 3) none of these compounds which hydrolyse at pH 8 showed any polarographic signs of hydrolysis of the dichloracetamido group.

It is of particular interest to note the polarograms of *N*-(4-nitrobenzyl)-*N*-(2-hydroxyethyl)dichloracetamide in that both the nitro group and the two chlorines of the dichloracetamido group are reduced polarographically in 50% methanol at pH 8 (Fig. 1). The freshly prepared solution of this compound results in three waves polarographically (Curve A in Fig. 1). The first is the reduction wave of the nitro group. The second and third waves result from the reduction of the individual chlorines of the dichloracetamido group. Curve B in Fig. 1 represents, polarographically, the same solution only after it had been set aside for 3 days at room temperature. Only two waves are present in this polarogram, the first being identical with the reduction wave of the nitro group in the fresh solution. The second wave does not have the polarographic characteristics of either the reduction wave of the chlorines of the dichloracetamido group but does have the same polarographic characteristics of dichloracetic acid in this medium.

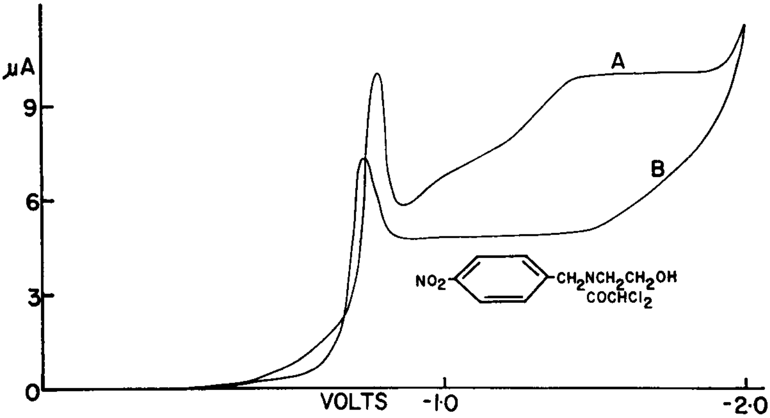


FIG. 1.—Polarograms of 0·0005*M* solutions in 50% methanol and pH 8 buffer:
A—fresh solution,
B—3-day old solution.

This is unequivocal evidence that the dichloracetamido group in the presence of a nitro group does contribute to the resulting polarogram of a freshly prepared solution in 50% methanol and pH 8, and that upon hydrolysis of the compound at room temperature that the dichloracetate ion contributes to the resulting polarogram along with the reduction wave of the nitro group.

With chloramphenicol {D(—)-threo-2,2-dichloro-*N*-[β-hydroxy-α-(hydroxymethyl)-*p*-nitrophenethyl]-acetamide}, in the same polarographic medium as above, three reduction waves result which are similar to those in Curve A in Fig. 1. After 3 days in this medium, the resulting polarogram is identical with the polarogram of the freshly prepared solution. This emphasises the stability of both the nitro and dichloracetamido groups in a compound not having a 2-hydroxyethyl group present on the amide nitrogen to initiate the hydrolysis of the dichloracetamido group at pH 8.

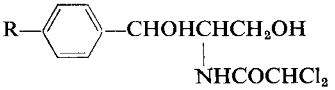
Group II

With the compounds in Group II only the aliphatic group attached to the sulphone or sulphide is varied. With the sulphone homologues, increasing the aliphatic chain from methyl to butyl results in a decrease in half-wave potentials (Table V), while with the sulphide homologues (Table V) an increase in half-wave potentials results.

Comparison of the sulphide, sulphoxide and sulphone analogues (numbers 28, 27, 22 in Table V) shows an increase of half-wave potential with an increase of oxygen content.

With certain isomeric compounds, polarography has shown a difference between the isomers. With the three available isomers of raceophenidol (dl, Dd, and Ll) there is no apparent difference in their polarograms at pH 3 or 8.

TABLE V.—POLAROGRAPHIC REDUCTION OF GROUP II COMPOUNDS IN BUFFERED 50% METHANOL



$R-C_6H_4-CHOH\underset{\underset{NHCOCHCl_2}{|}}{CH}CH_2OH$

	R	First wave		Second wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
22	CH_3SO_2—	1·04	1·62	1·45	1·50
23	$C_2H_5SO_2$—	0·97	1·51	1·41	1·38
24	$C_3H_7SO_2$—	0·93	2·12	1·41	2·04
25	$CH_2{=}CHCH_2SO_2$—	0·93	1·46	1·41	1·21
26	$C_4H_9SO_2$—	0·86	1·29	1·41	1·26
27	CH_3SO—	0·94	1·34	1·42	1·12
28	CH_3S—	0·66	1·30	1·40	*
29	C_2H_5S—	0·69	1·35	1·44	*
30	$CH_2{=}CHCH_2S$—	0·72	1·21	1·40	*
31	C_4H_9S—	0·74	1·47	1·34	*

* Second wave poorly defined.

Group III

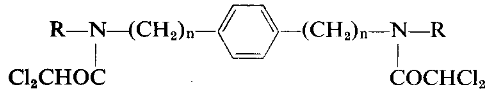
Compounds from the three other groups discussed in this communication dissolve readily in methanol while the compounds in Group III not only dissolve with difficulty but crystallise out of the buffered 50% methanol media within a short period of time at room temperature. This series did dissolve readily in *N*,*N*-dimethylformamide (DMF), but on mixing with the constant ionic strength buffers, the buffer constituents precipitated in the presence of 50% DMF. With less DMF the compound crystallises out of the media. On using a medium consisting of 70% methanol, 10% DMF and 20% water (containing the buffer) clear solutions with these Group III compounds result for at least 3 days at room temperature. Because of these solubility problems, polarograms were run only at pH 8·2. For a given compound of Group III, the half-wave potentials and the wave heights from the resulting polarograms are the same whether the medium is 70% methanol-10% DMF or the 50% methanol medium (before crystallisation of the compound occurs).

The half-wave potentials decrease about 0·3 V when the structure of the compound is changed from a secondary to a tertiary amide (Table VI).

With the tertiary amide series of compounds, the various substituents did not appreciably affect the polarographic characteristics of the given series of compounds when n = 1 or 0 (Table VI). If the benzene nucleus is replaced with cyclohexane, the polarographic characteristics are not altered appreciably.

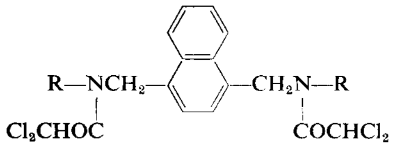
Compounds in Group III which possess the 2-hydroxyethyl group attached to the amide nitrogen, as was the case with chlorbetamide and related compounds in Group I, result in hydrolysis of the dichloracetamido groups. The 2-hydroxyethyl

TABLE VI.—POLAROGRAPHIC REDUCTION OF GROUP III COMPOUNDS IN BUFFERED 70% METHANOL-10% DMF

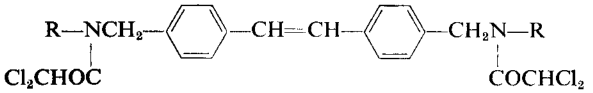


R		n	First wave		Second wave	
			$-E_{1/2}$	I	$-E_{1/2}$	I
32	—H	1	1·01	2·02	1·49	2·96
33	$—CH_3$	1	0·70	3·26	1·26	3·47
34	$—C_2H_5$	1	0·65	2·18	1·24	3·45
35	$—CH(CH_3)_2$	1	0·63	2·22	1·25	2·26
36	$—C_3H_7$	1	0·61	3·06	1·20	3·42
37	$—CH_2CH_2OH$	1	0·65	2·27	1·28	2·26
38	$—CH_2CH_2OC_2H_5$	1	0·66	3·33	1·22	3·36
39	$—CH_2CH_2OCOCH_3$	1	0·61	2·95	1·19	2·92
40	—H	0	Single drawn-out wave		1·19	7·70
41	$—CH_3$	0	0·69	2·82	1·21	3·98
42	$—C_2H_5$	0	0·67	2·94	1·23	3·73
43	$—CH(CH_3)_2$	0	0·69	3·07	1·28	3·99
44	$—CH(CH_3)(C_2H_5)$	0	0·64	3·51	1·27	4·29

TABLE VII.—POLAROGRAPHIC REDUCTION OF GROUP III COMPOUNDS IN BUFFERED 70% METHANOL-10% DMF



R		First wave		Second wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
45	$—C_2H_5$	0·56	3·07	1·17	3·52
46	$—C_2H_4OH$	0·62	3·22	1·24	3·08
47	$—C_2H_4OCH_3$	0·55	3·18	1·14	3·63



R		First wave		Second wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
48	$—CH_3$	0·47	3·12	1·15	3·36
49	$—C_2H_5$	0·47	3·29	1·15	3·42
50	$—CH(CH_3)_2$	0·47	3·21	1·15	3·42

compound (number 37 in Table VI) shows 77% hydrolysis after 3 days at room temperature and pH 8·2. The 2-acetoxyethyl analogue (number 39 in Table VI) shows only 15% hydrolysis under the same conditions. This emphasises again the necessity of the free 2-hydroxyethyl group to initiate the hydrolysis of the dichloracetamido group.

Replacement of the benzene nucleus with naphthalene (Table VII) does not change appreciably the general polarographic characteristics. The 2-hydroxyethyl compound (number 46 in Table VII), however, results in 60% hydrolysis of the dichloracetamido groups after 3 days at room temperature and pH 8·2.

Replacement of the benzene nucleus with stilbene results in a series of compounds (Table VII) which are all the same polarographically, even though the aliphatic substituents attached to the amide nitrogen are different.

Group IV

This series of *N,N'*-bis-(dichloracetyl)-polymethylenediamines presented the opportunity to study polarographically two homologous series, one with the secondary amide linkage and the other with the tertiary amide linkage of the dichloracetyl group.

With the secondary amide homologous series (Table VIII) the effect of increasing the distance between the two dichloracetamido groups by increasing the methylene groups from 2 to 9 is readily apparent. The half-wave potentials decrease (not linearly though) with the increasing number of methylene groups. The decamethylene homologue is not listed in this table because its first wave is entirely different from any other members of this series (or for that matter from any of the compounds studied). The half-wave potential of the first wave is —0·79 V and has the appearance of a reversible wave (very steep slope). The slope of the second wave (—1·24 V) is similar to the other members of the series (gradual change in slope).

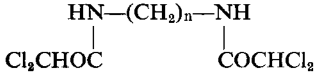
With the tertiary amide homologous series (Table IX) the presence of the ethyl group appears to nullify any appreciable change in the half-wave potentials of these methylene homologues (n = 4 to 12). The trend, however, is the opposite of the striking effect shown by the secondary amide series in that the half-wave potentials increase rather than decrease with the increasing number of methylene groups. It should be noted that with the tertiary amide series the half-wave potentials are 0·1 to 0·3 V lower than the corresponding secondary amide.

With the hexamethylene compounds (Table X) the various substitutions on the nitrogen result in very little change in the half-wave potentials of the two waves of the dichloracetamido groups. Only two of these compounds show, polarographically, hydrolysis of the dichloracetamido groups. Number 70 in Table X which contains the 2-hydroxyethyl group attached to the amide nitrogen and number 73 which contains a potentially available 2-hydroxyethyl group (2-acetoxyethyl analogue of number 70). Both of these compounds are hydrolysed 100% after 3 days at room temperature and pH 8, as determined polarographically by the presence of only the dichloracetate ion reduction wave.

Possible correlation between polarographic findings and biological effectiveness

Groups I, II and III. With the available data there is no clear-cut relationship between the biological activity of these compounds and their polarographic characteristics.[9,10,11,12]

TABLE VIII.—POLAROGRAPHIC REDUCTION OF GROUP IV COMPOUNDS IN BUFFERED 50% METHANOL



$$\underset{\mathrm{Cl_2CHOC}}{\mathrm{HN}}\mathrm{{-}(CH_2)_n{-}}\underset{\mathrm{COCHCl_2}}{\mathrm{NH}}$$

	n	First Wave		Second Wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
51	2	1·05	4·42	1·49	4·54
52	3	0·97	3·07	1·44	2·76
53	4	0·87	2·71	1·40	2·39
54	5	0·84	2·94	1·33	2·62
55	6	0·78	2·69	1·32	2·48
56	7	0·75	3·15	1·27	3·73
57	8	0·71	2·48	1·27	2·59
58	9	0·70	2·71	1·23	2·61

TABLE IX.—POLAROGRAPHIC REDUCTION OF GROUP IV COMPOUNDS IN BUFFERED 50% METHANOL

$$\underset{\mathrm{Cl_2CHOC}}{\mathrm{C_2H_5N}}\mathrm{{-}(CH_2)_n{-}}\underset{\mathrm{COCHCl_2}}{\mathrm{NC_2H_5}}$$

	n	First Wave		Second Wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
59	4	0·55	2·94	1·09	3·36
60	5	0·56	3·46	1·09	3·52
61	6	0·56	3·21	1·10	3·32
62	7	0·57	3·09	1·10	3·08
63	8	0·59	2·92	1·14	3·16
64	9	0·60	2·52	1·18	3·06
65	10	0·61	3·20	1·18	3·21
66	12	0·64	2·57	1·21	2·85

TABLE X.—POLAROGRAPHIC REDUCTION OF GROUP IV COMPOUNDS IN BUFFERED 50% METHANOL

$$\underset{\mathrm{Cl_2CHOC}}{\mathrm{R{-}N}}\mathrm{(CH_2)_6{-}}\underset{\mathrm{COCHCl_2}}{\mathrm{N}}\mathrm{{-}R}$$

	R	First Wave		Second Wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
67	—H*	0·78	2·69	1·32	2·48
68	$—CH_3$	0·55	2·76	1·08	2·66
69	$—C_2H_5$†	0·56	3·21	1·10	3·32
70	$—C_2H_4OH$	0·57	2·31	1·16	2·74
71	$—C_2H_4OCH_3$	0·57	2·70	1·13	3·10
72	$—C_2H_4OC_2H_5$	0·57	2·45	1·18	2·86
73	$—C_2H_4OCOCH_3$	0·51	2·43	1·09	2·85

* This is the same compound as number 55 in Table VIII.

† This is the same compound as number 61 in Table IX.

Group IV. With the homologous series of the secondary amide compounds (Table VIII), when n = 2, 3, 4, 5, 6, 7, 9 or 10 the compounds possess amebicidal activity. This amebicidal activity is found to increase with the increase in the number of methylene groups between the two dichloracetamido groups.[13] Polarographically, the half-wave potentials of the first reduction wave of the dichloracetamido group decrease, though not linearly with the increase in the number of methylene groups. When n is 8, however, the amebicidal activity is very low. On the other hand, this homologue (number 57 in Table VIII) has proved to possess the most effective antispermatogenic activity of all of the compounds yet tested in either Group III or IV.[12,13,14] Why the octamethylene homologue has such a singular potency as a spermatocide remains unanswered because the homologues (n = 7 or 9) have little such activity. Polarographically, one does note a uniqueness with the octamethylene compound in that it shows a sharply defined prewave (at 0·71 V) before the first reduction wave. None of the other homologues shows this polarographic characteristic.

With the tertiary amide series (Table IX), even though there is no consistent relationship between the length of the methylene chain and amebicidal activity, they possess (as a group) the greater amebicidal activity on comparing with the secondary amide compounds.[13] Polarographically, the half-wave potentials resulting from the reduction of the first chlorine of the dichloracetamido group in the tertiary amide series are 0·1 to 0·3 V lower than those from the secondary amide compounds.

With the various analogues of the hexamethylene series (Table X) there is little change in amebicidal activity.[13] These different R-groups had little effect on the polarographic characteristics of these analogues.

CONCLUSION

Because the first reduction wave of the chlorine from the dichloracetamido group is so well-defined, its wave height may be utilised in measuring quantitatively the amount of intact dichloracetamido compound in various pharmaceutical formulations (chiefly tablets, injections and feed premixes). The values obtained were within ±2% of label claim. The resulting polarograms, during a stability testing programme, of 1 year, were especially helpful in proving conclusively that the dichloracetamido group is stable in the pharmaceutical preparation as shown by the absence of the dichloracetate reduction wave.

Zusammenfassung—An verschiedenen Verbindungen, die dic Dichloracetamidogruppe enthalten, wie N-(2,4-dichlorbenzyl-)N-(2-hydroxyäthyl-) dichloracetamid (Chlorbetamid), N-(4-methylsulfonylphenyl-) 1,3-dihydroxy-2-propyl-dichloracetamid (Raceophenidol), N,N′-bis-(2-äthoxyäthyl-)N,N′-p-xylylen-bisdichloracetamid (Teclozan), N,N′-octamethylen-bisdichloracetamid und analogen Verbindungen, wurden polarographische Untersuchungen angestellt. Die analytischen Ergebnisse werden vom quantitativen und qualitativen Gesichtspunkt aus diskutiert, mit besonderem Nachdruck auf der Stabilität der Verbindungen bei verschiedenen p_H-Werten und auf dem Einfluß verschiedener Elemente oder Gruppen im Molekül auf die Halbwellenpotentiale der beiden kathodischen Wellen.

Résumé—L'auteur a étudié par polarographie une série de composés contenant des groupes dichloroacétamide comprenant N-(2,4-dichlorobenzyl)-N-(2-hydroxyéthyl)dichloroacétamide (chlorbetamide),

N-(4-méthylsulfonylphényl)-1,3-dihydroxy-2-propyl-dichloroacétamide (raceophenidol), N,N′-bis-(2-éthoxyéthyl)-N,N′-p-xylylène-bis-dichloroacétamide (teclozan), N,N′-octaméthylène-bis-dichloroacétamide et leurs analogues. Les résultats analytiques sont discutés du point de vue qualitatif et quantitatif en insistant particulièrement sur la stabilité de ces composés à différents pH et sur l'influence des éléments ou des groupes variés situés dans la molécule sur les potentiels de demi-vague des deux vagues de réduction.

REFERENCES

[1] G. B. Hess, *Analyt. Chem.*, 1950, **22**, 649.
[2] G. Varela, *Microbiol. expanola*, 1951, **4**, 39.
[3] E. Knobloch and E. Svatek, *Coll. Czech. Chem. Comm.*, 1955 **20**, 1113.
[4] P. J. Elving and Ching-Siang Tang, *J. Amer. Chem. Soc.*, 1950, **72**, 3244.
[5] *Idem, Analyt. Chem.*, 1951, **23**, 341.
[6] *Idem, J. Amer. Chem. Soc.*, 1952, **74**, 6109.
[7] P. J. Elving, J. M. Markowitz and I. Rosenthal, *Analyt. Chem.*, 1956, **28**, 1179.
[8] G. W. C. Milner, *The Principles and Applications of Polarography.* Longmans, Green and Co., London, 1957, p. 105.
[9] A. R. Surrey, *J. Amer. Chem. Soc.*, 1954, **76**, 2214;
A. R. Surrey and M. K. Rukwid, *ibid.*, 1955, **77**, 3798;
A. R. Surrey, G. Y. Lesher and S. O. Winthrop, *ibid.*, 1955, **77**, 5406;
A. R. Surrey and G. Y. Lesher, *ibid.*, 1956, **78**, 2573;
A. R. Surrey, A. J. Olivet, S. O. Winthrop and G. Y. Lesher, *ibid.*, 1956, **78**, 3834.
[10] W. F. Warner and R. A. Cutler, *Bacteriol. Proc.*, 1954, 79.
[11] D. A. Berberian, R. G. Slighter and A. R. Surrey, *Antibiot. Chemotherapy*, 1961, **11**, 245.
[12] A. R. Surrey and J. R. Mayer, *J. Med. Pharm. Chem.*, 1961, **3**, 409.
[13] *Idem, ibid.*, 1961, **3**, 419.
[14] A. L. Beyler, G. O. Potts, F. Coulston and A. R. Surrey, *Endocrinol.*, 1961, **69**, 819.

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SCHIFF BASE COMPLEXES

A NUMERICAL STUDY OF THE NICKEL^{II}—PYRUVATE—GLYCINATE SYSTEM USING A HIGH SPEED COMPUTER*

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Summary—A numerical study of the nickel^{II}-pyruvate-glycinate system is undertaken and a computer method of solving the pertinent equations is developed. Theoretical titration curves using trial constants are calculated for conditions corresponding to those used experimentally. The observed inter-relationships between the values of the constants, the concentrations of the reactants and the resulting titration curves yield valuable information regarding the importance of the various mixed complexes under the differing conditions. The "best" set of constants which fits the experimental data according to the minimum value of the sum of the squares of the residuals, $pH_{calc}\ i - pH_{obs}\ i$, is obtained. The results of the study lead to a procedure which should be applicable to determining the constants for mixed complex systems in general.

SCHIFF base complexes partake in many interesting reactions. Pfeiffer and coworkers[1] have demonstrated that enhanced rates of ester exchange and hydrolysis and oxidative de-amination can occur in these systems. The paramagnetic and diamagnetic properties of the nickel^{II} complexes have recently come under intensive study.[2,3] The investigations of Krumholz,[4a] Figgins and Busch[4b,c] and Blight and Curtis[4d] have resulted in interesting compounds having unusual properties. Of special importance is the role these complexes play in non-enzymatic transamination.[5,6,7,8,9] In order to understand more completely the behaviour of Schiff base co-ordination compounds it is desirable to extend our knowledge of the compositions and stabilities of the complexes formed in solution. Such information is a prerequisite to the complete understanding of any equilibrium or kinetic properties of these systems.

One difficulty in the study of equilibria involving Schiff base complexes is the dissociation of the Schiff base itself,[10] *i.e.*, in addition to the Schiff base-metal ion equilibria, there is superimposed the equilibrium between the Schiff base and its component amine and carbonyl compounds. In one approach to the problem a recent communication[11] points out the value of treating these species as "mixed complexes" and using the Bjerrum titration method[12] to obtain the data. In this earlier paper, which concerns the nickel^{II}-pyruvate-glycinate system, Watters' method[13] of obtaining the concentrations of combined and uncombined glycinate was used. This method was feasible because a large difference exists in the basicities of the pyruvate and glycinate ions, and the nickel^{II} "mixed complexes" form predominantly under conditions of pH where pyruvic acid is almost completely dissociated and uncombined glycine is ionized to only a very slight extent. An iterative procedure was used to obtain the formation constants of the species NiPG, $NiPG_2^-$ and $NiP_2G_2^{2-}$ (P^- = pyruvate, G^- = glycinate).

In those systems where the "mixed complexes" are formed under conditions

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* Presented in part before the 145th National ACS Meeting, New York, 1963.

where appreciable concentrations of undissociated pyruvic acid are present, Watters' method does not apply. This was found to cause minor difficulties even in the present study and produces a more severe interference when the complexes of copper^{II} are under investigation. Also, in systems of considerable interest, such as those involving pyridoxal or salicylaldehyde and its derivatives, the acidities of the carbonyl compounds approach those of the amino acids, completely obviating Watters' method.

In the present study employing an IBM 7090 computer a numerical investigation of the inter-relationships between the experimental parameters, the concentrations of metal, pyruvate and glycinate ions, the values of the complex formation constants and the shapes of the titration curves, was undertaken. The results led to a general method of obtaining the "best" constants according to a least-squares fit for such systems, and also rendered valuable insight into their equilibrium properties. While the method described below concerns one particular system it can be applied directly to other metal ion-ketoacid-amino acid systems and, with only slight modifications, should even be applicable to those more complicated situations where pyridoxal is involved.

OUTLINE OF COMPUTATIONAL METHOD

In the experiments, solutions containing complexing metal ions, pyruvic acid, sodium pyruvate and inert electrolyte in known concentrations were titrated with a sodium glycinate solution and the equilibrium values of pH were measured after each addition of titrant. A series of titration curves was obtained using solutions with different initial concentrations. The formation constants of the simple complexes, the acid dissociation constants of the ligands and their Schiff base formation constant were determined from the results of similar, separate experiments.

In the computation all of these data, including observed points (pH *vs.* ml) from the experimental titration curves, and the initial concentrations of reactants are first read into and stored in the computer. A predetermined network of trial values of the formation constants of the mixed complexes is then systematically scanned. For each set of constants a theoretical titration curve is calculated pertaining to each of the initial conditions. The residual, pH_{calc}–pH_{obs}, is obtained for each of the observed points and the quantity U, which is the sum of the squares of the residuals over all of the points, is computed.

Residuals in pH were minimised because values of pH are measured directly while in mixed complex systems the derived quantity $\bar{n}$, which is more commonly used in calculating equilibrium constants, is not single-valued with regard to the experimental variables, volume and pH. Furthermore, weighting procedures, which may be somewhat involved when $\bar{n}$ values are used,[14] are simplified because each point can be given unit weight. The error is assumed to lie entirely in the measured value of pH and the volume is assumed to be accurately known.

If a sufficiently broad network of constants has been used the region where the minimum value of U lies can be located and passing finer and finer networks through this region the constants which best fit the data can be obtained to the appropriate degree of accuracy. When the calculated $N + 1$ dimensional surface (N is the number of equilibrium constants being evaluated) is sufficiently wrinkled it is possible for the compution to converge on a "false minimum". One of the purposes of the present approach was to determine if such false minima are apt to interfere with obtaining the "best fit" for these systems.

Considering the bidentate character of pyruvate and glycinate, the tridentate character of their Schiff base and the predominant hexadentate character of the transition metal ions of the first series, the mixed complexes MPG, MP_2G^-, MPG_2^- and MP_2G^{2-} are expected. Considering also the simple species, mass-conservation leads to the following set of equations:

$$\begin{aligned} M_t = {} & (M^{2+}) + (MP^+) + (MP_2^0) + (MG^+) + (MG_2^0) + (MG_3^-) + (MPG) \\ & + (MP_2G^-) + (MPG_2^-) + (MP_2G_2^{2-}) \end{aligned} \tag{1}$$

$$\begin{aligned} P_t = {} & (HP) + (P^-) + (MP^+) + 2(MP_2^0) + (MPG) + 2(MP_2G^-) + (MPG_2^-) \\ & + 2(MP_2G_2^{2-}) + (PG^{2-}) \end{aligned} \tag{2}$$

$$\begin{aligned} G_t = {} & (H_2G^+) + (HG^\pm) + (G^-) + (MG^+) + 2(MG_2^0) + 3(MG_3^-) + (MPG) \\ & + (MP_2G^-) + 2(MPG_2^-) + 2(MP_2G_2^{2-}) + (PG^{2-}) \end{aligned} \tag{3}$$

$$H_t = 2(H_2G^+) + (HG^\pm) + (HP) + (H^+) - (OH^-) \tag{4}$$

where the quantities on the left-hand side are the known concentrations of complexing metal ions, pyruvate, glycinate and replaceable hydrogen ions and those on the right-hand side are the concentrations of the various species.

Defining the over-all formation constant of the complex MP_pG_g as

$$Q_{pg} = \frac{(MP_pG_g)}{(M)(P^-)^p(G^-)^g}$$

and the formation constant of the Schiff base PG^{2-} as Q_{SB}, substitution into equations (1)–(4) gives:

$$\begin{aligned} M_t = {} & (M^{2+})[1 + Q_{10}(P^-) + Q_{20}(P^-)^2 + Q_{01}(G^-) + Q_{02}(G^-)^2 + Q_{03}(G^-)^3 \\ & + Q_{11}(P^-)(G^-) + Q_{21}(P^-)^2(G^-) + Q_{12}(P^-)(G^-)^2 + Q_{22}(P^-)^2(G^-)^2] \end{aligned} \tag{5}$$

$$\begin{aligned} P_t = {} & \left[\frac{a_H}{Kap} + 1\right](P^-) + Q_{10}(M^{2+})(P^-) + 2Q_{20}(M^{2+})(P^-)^2 + Q_{11}(M^{2+})(P^-)(G^-) \\ & + 2Q_{21}(M^{2+})(P^-)^2(G^-) + Q_{12}(M^{2+})(P^-)(G^-)^2 + 2Q_{22}(M^{2+})(P^-)^2(G^-)^2 \\ & + Q_{SB}(P^-)(G^-) \end{aligned} \tag{6}$$

$$\begin{aligned} G_t = {} & \left[\frac{a_H{}^2}{K_{1aG}K_{2aG}} + \frac{a_H}{K_{2aG}} + 1\right](G^-) + Q_{01}(M^{2+})(G^-) + Q_{02}(M^{2+})(G^-)^2 \\ & + Q_{03}(M^{2+})(G^-)^3 + Q_{11}(M^{2+})(P^-)(G^-) + Q_{21}(M^{2+})(P^-)^2(G^-) \\ & + 2Q_{12}(M^{2+})(P^-)(G^-)^2 + 2Q_{22}(M^{2+})(P^-)^2(G^-)^2 + Q_{SB}(P^-)(G^-) \end{aligned} \tag{7}$$

$$H_t = \frac{a_H(P^-)}{K_{ap}} + \left[\frac{2a_H{}^2}{K_{1aG}K_{2aG}} + \frac{a_H}{K_{2aG}}\right](G^-) + (H^+) - (OH^-) \tag{8}$$

In equation (8) a_H refers to the hydrogen ion activity whereas (H^+) is the concentration. From blank titrations of the inert electrolyte with hydrochloric acid solutions it was found that $(H^+) = a^{0.96}$ and this relationship was used to make the correction iteratively for free (H^+).

In the experiments, the values of M_t, P_t and H_t are known at each point on the titration curve from the initial concentration and the dilution factor. The value of G_t is also known from the concentration of NaG in the titrant and the volume added.

However, in computing the theoretical curves, because of the higher order equations involved, it is simpler to begin with a value of (G^-) and from this to calculate the corresponding values of pH and G_t than it is to calculate the values of pH and G^- using G_t. Accordingly, the above equations are rearranged in terms of (G^-) and the unknowns (P^-) and a_H.

Solving equation (5) for (M^{2+}) and substituting into equation (6) gives, on rearrangement,

$$F(P^-) = C_3(P^-)^3 + C_2(P^-)^2 + C_1(P^-) - S_0P_t \tag{9}$$

where $C_3 = C_0S_2$

$$C_2 = C_0S_1 + (2M_t - P_t)S_2$$
$$C_1 = C_0S_0 + (M_t - P_t)S_1$$
$$C_0 = a_H/K_{ap} + Q_{SB}(G^-) + 1$$
$$S_1 = Q_{10} + Q_{11}(G^-) + Q_{12}(G^-)^2$$
$$S_2 = Q_{20} + Q_{21}(G^-) + Q_{22}(G^-)^2$$
$$S_0 = 1 + Q_{01}(G^-) + Q_{02}(G^-)^2 + Q_{03}(G^-)^3$$

and the quantities S_i are polynomials depending only on (G^-) and the formation constants.

The correct solution for a given value of G^- is that positive value of (P^-) (and a_H) which causes $F(P^-)$ to become equal to zero.

The value of a_H can be obtained in terms of (G^-) and (P^-) using the quadratic equation

$$a_H = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \tag{10}$$

where, from equation (8),

$$a = 2(G^-)/K_{1aG}K_{2aG},$$
$$b = (G^-)/K_{2aG} + (P^-)/K_{ap},$$
$$c = a^{0.96} - H_t.$$

The positive root is used because the quantity a_H must be positive.

Once the value of (G^-) is chosen, equation (9) and (10) become two non-linear equations in two unknowns. The equations are solved as follows. First (P^-) is set equal to zero and the corresponding value of a_H is calculated from equation (10) [iteratively when the term resulting from free (H^+) is appreciable with regard to H_t]; these values of a_H and (P^-) are inserted into equation (9) to give a value of $F(P^-)$; (P^-) is incremented by some predetermined amount (usually of the order 0·1 to 0·2 P_t) and a new value of $F(P^-)$ is similarly obtained. A test is made to determine if $F(P^-)$ has changed sign. This process is repeated until a sign change in $F(P^-)$ indicates that a root of equation (9) has been reached. The values of (P^-) and a_H are then refined iteratively using the Newton-Raphson[15] method until any change in (P^-) is less than 0·2% of its value at that time. A test is made to verify that a_H is positive. A negative value signifies an incorrect root and (P^-) is again successively incremented until $F(P^-)$ once more changes sign. In practice it has been observed that the correct root lies at the first sign change. The reason for this can be seen in the data of Table I where $F(P^-)$ and a_H have been computed for various conditions. Only one root appears to exist in the range $0 \leq P^- \leq P_t$. In the region of interest $F(P^-)$ is a smooth curve for which the first, second and third derivatives are all positive. The last appears to be about constant. No troublesome convolutions nor inflections exist in the region $F(P^-) = 0$. Also, it can be seen that any error in pH caused by a 0·2% uncertainty in (P^-) has negligible proportions as far as the present purposes are concerned.

Using the chosen value of (G^-) and those obtained for (P^-) and a_H, (M^{2+}) is evaluated from equation (5) and using these results in equation (7), G_{tcalc} is calculated. The volume of titrant necessary to give this value of G_{tcalc} is obtained from the experimentally known concentration of the titrant and the initial volume. The values of M_t, P_t and H_t are corrected for dilution and the last is also corrected for the effect of any excess sodium hydroxide in the titrant. The entire calculation is repeated iteratively until changes in H_t amount to less that 0·2% of its value. In this way one theoretical point on the titration curve (pH *vs.* ml) is obtained. To obtain another point, the value of $-\log(G^-)$ is increased. The final titration curve results when the desired range of (G^-) values has been covered. The time taken to compute one point is of the order of 25 msec with the IBM 7090 computer.

Only by rare coincidence does an observed and computed volume of titrant agree. Therefore, to obtain the residual for each observed volume it is necessary to interpolate. A second order LaGrange interpolation[16] is performed. Three calculated points bracketing each observed point are used in the interpolation. In the region of interest where the mixed complexes are formed, the buffer capacity of the solutions is large and a higher order equation is not necessary for the interpolation.[17]

The computed points are printed out and the next set of experimental conditions is taken. When the computation for the final experiment has been performed the value of U is also printed out. A new set of constants is then taken. With the IBM 7090 computer the time required to compute a theoretical curve of 16 points, interpolate and obtain the sum of the squares of the residuals is less than 0.6 sec.

In the first version of the programme the constants were varied from initial to final values in fixed steps. To save computer time all of the titration curves were not computed for a given combination of constants if it was found that at any point the absolute value of a residual was greater that 0·15 pH unit. The programme was designed to cease calculations at this point and go on to the next set of constants. Furthermore, because the constants were varied from low to high values, shifting the computed curves to more acid values as the computation progressed, a particular region was considered to be out of range of interest and was no longer investigated if a point on a calculated curve was found to become more acid by 0·15 pH unit than the corresponding experimental point.

DATA AND RESULTS FOR THE NICKEL^{II} PYRUVATE-GLYCINATE SYSTEM

The data from which the $\bar{n}_G$ and $\log(G^-)$ values reported in reference 11 were calculated was taken. In these experiments solutions which contained either 0·0500*M* $NiCl_2$, 0·0500*M* pyruvic acid, (I); 0·0500*M* $NiCl_2$, 0·0500*M* pyruvic acid, 0·0550*M* sodium pyruvate, (II); 0·0500*M* $NiCl_2$, 0·0500*M* pyruvic acid, 0·100*M* sodium pyruvate, (III); 0·0220*M* $NiCl_2$, 0·0500*M* pyruvic acid and 0·100*M* sodium pyruvate, (IV) were prepared. These solutions also contained sufficient potassium chloride to bring the ionic strength to 0·70. Twenty-five ml aliquots were titrated at 25·0° with 0·800*M* sodium glycinate. The pH measurements were made with a Radiometer pHM22 pH meter with a scale expander. Readings were made to the nearest 0·005 pH

TABLE I.—VALUES OF a_H AND THE FUNCTION $F(P^-)_G$
($Q_{11} = 1{\cdot}25 \times 10^8$, $Q_{12} = 1{\cdot}00 \times 10^{13}$, $Q_{21} = 0$, $Q_{22} = 2{\cdot}00 \times 10^{15}$)

Expt. no.	Log (G^-) = 6·50				Log (G^-) = 5·00			
(P^-), *moles. litre*	$a_H \times 10^5$	$F(P^-)_G$	$\Delta^1F(P^-)_G$	$\Delta^2F(P^-)_G$	$a_H \times 10^7$	$F(P^-)_G$	$\Delta^1F(P^-)_G$	$\Delta^2F(P^-)_G$
0·00000	2·820	−0·05229			8·5313	−0·38359		
			0·01257				0·77957	
0·00750	2·817	−0·03973		0·00773	8·5309	+0·39598		1·7482
			0·02030				2·5277	
0·01500	2·814	−0·01943		0·00824	8·5306	2·9237		2·2545
			0·02854				4·7823	
0·02250	2·810^5	+0·00911		0·00875	8·5303	7·7060		2·7609
			0·03729				7·5432	
0·03000	2·807	0·04639		0·00926	8·5300	15·5249		3·2673
			0·04654				10·810	
0·03750	2·804	0·09294		0·00977	8·5297	26·060		3·7736
			0·05631				14·584	
0·04500	2·801	0·14925		0·01028	8·5293	40·644		
			0·06659					
0·05250	2·798	0·21584						
Expt. no. III	Log (G^-) = 6·50				Log (G^-) = 5·00			
0·00000	2·691	−0·15353			8·1497	−1·1283		
			−0·02457				−1·6109	
0·00750	2·688	−0·17839		0·00570	8·1494	−2·7392		−0·1687
			−0·01915				−1·7796	
0·01500	2·685	−0·19754		0·00621	8·1491	−4·5188		+0·3377
			−0·01294				−1·4419	
0·02250	2·682	−0·21048		0·00672	8·1489	−5·9607		0·8440
			−0·00622				−0·5979	

TABLE 1 (*Continued*)

Expt. no. III	Log $(G^-) = 6{\cdot}50$				Log $(G^-) = 5{\cdot}00$			
0·03000	2·679	−0·21670		0·00723	8·1485	−6·5585		1·3504
			+0·001011				+0·7525	
0·03750	2·676	−0·21569		0·00774	8·1483	−5·8060		1·8568
			0·008751				2·6093	
0·04500	2·673	−0·20694		0·00825	8·1479	−3·1967		2·3631
			0·01700				4·9724	
0·05250	2·670	−0·18994		0·00876	8·1477	+1·7757		2·8695
			0·02576				7·8419	
0·06000	2·667	−0·16418		0·00927	8·1473	9·6176		3·3759
			0·03503				4·218	
0·06750	2·664	−0·12915		0·00978	8·1470	20·835		3·8822
			0·04481				15·100	
0·07500	2·661	−0·084343		0·01209	8·1468	35·935		4·3886
			0·05510				19·489	
0·08250	2·658	−0·029248		0·01080	8·1464	55·424		4·8949
			0·06589				24·383	
0·09000	2·655	+0·036643		0·01131	8·1461	79·807		5·4013
			0·07197				29·785	
0·09750	2·652	0·11384		0·01182	8·1458	109·59		5·9077
			0·08901				35·692	
0·10500	2·649	0·20285		0·01232	8·1455	145·28		6·4140
			0·10134				42·106	
0·11250	2·646	0·30419		0·01283	8·1452	187·39		6·9204
			0·11417				49·027	
0·12000	2·643	0·41836			8·1449	236·42		

unit. National Bureau of Standards buffers were used to standardise the glass and calomel electrodes. In the titration curves only those points in the buffer regions where the mixed complexes form, were used in the calculations. As the concentration of pyruvate increases a pronounced break in the titration curve appears where the $Ni^{II}:(G^-)$ ratio is 1:2. This break is informative as far as the stoichiometry is concerned but the points close to the end-point have only slight value as far as determining the constants is concerned.

The constants for the formation of the simple nickel^{II}-glycinate complexes were found to be $4 \cdot 6 \times 10^5$, $3 \cdot 2 \times 10^{10}$ and $9 \cdot 0 \times 10^{13}$ for Q_{01}, Q_{02} and Q_{03}, respectively. For the nickel^{II}-pyruvate system Q_{10} was found to be 14. No evidence for the existence of NiP_2 was observed. The Schiff base formation constant was found to have a value of 2·2–2·3 from the results of a potentiometric titration of glycine in the presence of pyruvate with a solution of sodium hydroxide. This value compares favourably with 2·47 obtained polarographically by Zuman.[18] The value found for the acid dissociation constant of pyruvic acid, K_{aP}, is $4 \cdot 07 \times 10^{-3}$ while K_{1aG} and K_{2aG} for glycine were found to be $3 \cdot 4 \times 10^{-3}$ and $2 \cdot 0 \times 10^{-10}$.

In the previous communication[11] the values reported for Q_{11}, Q_{12} and Q_{22} are $1 \cdot 15 \times 10^8$, $2 \cdot 5 \times 10^{13}$ and $1 \cdot 6 \times 10^{15}$. Ordinarily these results would not be available in which case it is desirable, but not necessary, to make quick preliminary desk calculations to obtain the likely approximate values of the mixed complex formation constants. It is convenient to initiate the computations with the high speed computer using a network of constants with points spaced from about one-third to one-half the preliminary values. In the present series, Q_{11} was first varied from 0 to $3 \cdot 0 \times 10^8$ in steps of $0 \cdot 5 \times 10^8$, Q_{12} was varied from 0 to $4 \cdot 9 \times 10^{13}$ in steps of $0 \cdot 7 \times 10^{13}$ and Q_{22} was varied from 0 to $4 \cdot 5 \times 10^{15}$ in steps of $0 \cdot 5 \times 10^{15}$. Because Q_{20} was found to have a negligibly small value, it seemed reasonable that the same is also likely for Q_{21}. Therefore, in the first series of calculations Q_{21} was set equal to zero.

Complete sets of computed titration curves and values of U were obtained for only a relatively small region of the vector space of trial constants scanned because points for most of the computed curves fell outside the 0·15 pH unit limit. The results are shown in Table IIA. A finer network was then used to obtain the results given in Table IIB.

A final run was made using initial values $Q_{11} = 1 \cdot 15 \times 10^8$, $Q_{12} = 0 \cdot 8 \times 10^{13}$ and $Q_{22} = 1 \cdot 8 \times 10^{15}$, with increments $dQ_{11} = 0 \cdot 10 \times 10^8$, $dQ_{12} = 0 \cdot 20 \times 10^{13}$ and $dQ_{22} = 0 \cdot 20 \times 10^{15}$. The minimum value of U was found to be 0·0229 (43 points)[19] lying at $Q_{11} = 1 \cdot 25 \times 10^8$, $Q_{12} = 1 \cdot 0 \times 10^{13}$ and $Q_{22} = 2 \cdot 0 \times 10^{15}$. A plot of the points obtained for this last set of constants is given in Fig. 1 along with the observed values.

At this stage attempts were made to improve the fit by scanning a four dimensional array of constants using relatively small values of Q_{21} of the order of 10^9. These attempts resulted only in increased U values so it is concluded that as far as the present experimental conditions are concerned any effect of NiP_2G^- is negligible.

It is important to establish whether or not the values found above are meaningful or merely reflect the uncertainties in the pH measurements. Sillén[20] has described methods for obtaining the standard deviations of the constants and the observed points in cases such as the present, where the sum square surface has been obtained. After Sillén[20] a generalised four dimensional paraboloid was fitted to the displacements

TABLE II.—VALUES OF THE SUM-SQUARE AS A FUNCTION OF THE TRIAL CONSTANTS

A. Coarse network[a]

	$Q_{22} = 1{\cdot}50 \times 10^{15}$				$Q_{22} = 2{\cdot}0 \times 10^{15}$				$Q_{22} = 2{\cdot}5 \times 10^{15}$	
$Q_{11} \diagdown Q_{12}$	0[c]	7	14	21	0	7	14	21	0	7
0·0[b]	—	—	—	—	—	—	—	—	—	—
1·0	—	0·118	0·114	—	0·174	0·054	0·140	—	0·183	—
1·5	—	—	0·194	—	—	0·101	0·047	—	—	—
2·0	—	—	—	—	—	—	—	—	—	—

B. Medium network[a]

	$Q_{22} = 1{\cdot}50 \times 10^{15}$				$Q_{22} = 1{\cdot}70 \times 10^{15}$				$Q_{22} = 1{\cdot}90 \times 10^{15}$			
$Q_{11} \diagdown Q_{12}$	7[c]	10	13	16	7	10	13	16	7	10	13	16
1·00[b]	0·118	0·094	0·105	0·134	0·062	0·059	0·086	0·135	0·049	0·062	0·103	0·162
1·20	—	0·110	0·088	0·094	0·079	0·043	0·040	0·062	0·036	0·019	0·031	0·065
1·40	—	—	0·153	0·132	—	0·102	0·071	0·068	0·095	0·048	0·035	0·044
1·60	—	—	—	—	—	—	·0102	0·133	—	0·134	0·096	0·085
1·80	—	—	—	—	—	—	—	—	—	—	—	0·175

	$Q_{22} = 2{\cdot}10 \times 10^{15}$				$Q_{22} = 2{\cdot}30 \times 10^{15}$				$Q_{22} = 2{\cdot}50 \times 10^{15}$
$Q_{11} \diagdown Q_{12}$	7[c]	10	13	16	7	10	13	16	
1·00[b]	0·065	0·092	0·142	—	0·104	0·142	—	—	
1·20	0·028	0·026	0·050	—	0·046	0·056	—	—	
1·40	0·060	0·030	0·031	—	0·055	0·039	—	—	All out of range
1·60	—	0·091	0·069	—	0·118	0·078	—	—	
1·80	—	—	0·155	—	—	0·164	—	—	

[a] Values of the sum-square were printed out for only those sets of data for which the condition $-0{\cdot}15 \leq \mathrm{pH_{calc}} - \mathrm{pH_{obs}} \leq 0{\cdot}15$ is satisfied for all points on the computed titration curves. A total of 41 points was used in this series of calculations.

[b] $Q_{11} \times 10^{-8}$.

[c] $Q_{12} \times 10^{-13}$.

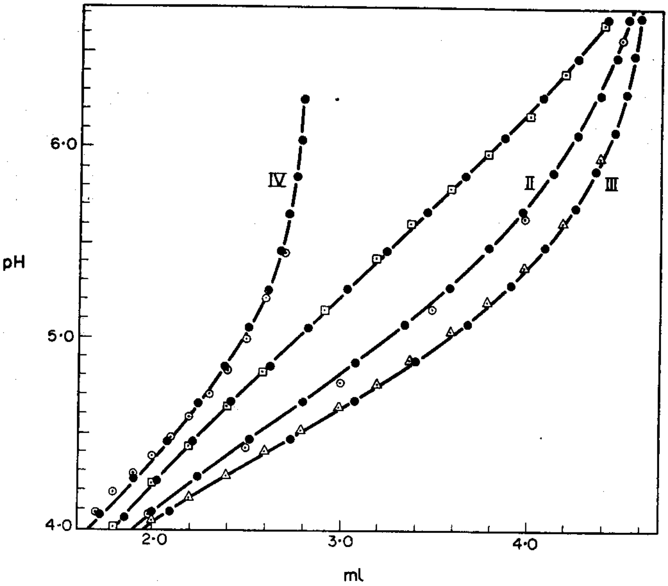

FIG. 1.—Computed and Observed Titration Curves.
The roman numerals refer to the experiment number given in the text. The open points are observed and the solid points are computed. The values used in the computation are $Q_{11} = 1{\cdot}25 \times 10^{+8}$, $Q_{12} = 1{\cdot}0 \times 10^{+13}$ and $Q_{13} = 2{\cdot}0 \times 10^{+15}$.

in U and in the constants for the last set of calculations taking the observed minimum where $U = 0{\cdot}0229$ as the origin. This gave the equation

$$U = 0{\cdot}0299 + 0{\cdot}0205 \times 10^{-8}x_1 + 0{\cdot}825 \times 10^{-16}x_1^2 - 0{\cdot}0035 \times 10^{-13}x_2 + 0{\cdot}155 \times 10^{-26}x_2^2 + 0{\cdot}0075 \times 10^{-15}x_3 + 0{\cdot}345 \times 10^{-30}x_3^2 - 0{\cdot}445 \times 10^{-21}x_1x_2 - 0{\cdot}625 \times 10^{-23}x_1x_3 + 0{\cdot}280 \times 10^{-28}x_2x_3$$

where $x_1 = Q_{11} - 1{\cdot}25 \times 10^{+8}$, $x_2 = Q_{12} - 1{\cdot}0 \times 10^{+13}$ and $x_3 = Q_{22} - 2{\cdot}0 \times 10^{+15}$. The surface defined by this equation is calculated to have a minimum, $U_{\min}$, equal to 0·0225. Because the values of three constants have been obtained losing three degrees of freedom the standard deviation of the points is calculated to be $\pm 0{\cdot}0225/(43-3) = \pm 0{\cdot}024$. This deviation is only slightly larger than the expected 0·01 — 0·02 unit uncertainty in the measured pH values. From the matrix of the coefficients of the displacements, the constants at the minimum and their standard deviations are calculated to be $Q_{11} = 1{\cdot}23 \pm 0{\cdot}04 \times 10^{+8}$, $Q_{12} = 1{\cdot}01 \pm 0{\cdot}08 \times 10^{+13}$ and $Q_{22} = 1{\cdot}97 \pm 0{\cdot}05 \times 10^{+15}$. The standard deviations are well below the values of the constants.

It is also worthwhile to make plots of various computed curves. In this way visual evidence may be obtained regarding the effects which given species have on the measured parameters under different conditions. This information is valuable in the design of experiments. In Fig. 2 are plotted the curves which were obtained using several values of Q_{11}, Q_{12} and Q_{22} for conditions pertaining to experiments I and II. Here it is seen that curve I is sensitive to the values of Q_{11} and Q_{12}, but the variation in Q_{22} has a negligible effect. On the other hand, curve III shows only a slight dependence on the value of Q_{12} but is shown to depend primarily on Q_{11} and Q_{22}. Thus, under the conditions of experiment (I) NiPG and $NiPG_2^-$ are indicated to be important, whereas in experiment (III) $NiP_2G_2^{2-}$ replaces the latter species. For more quantitative

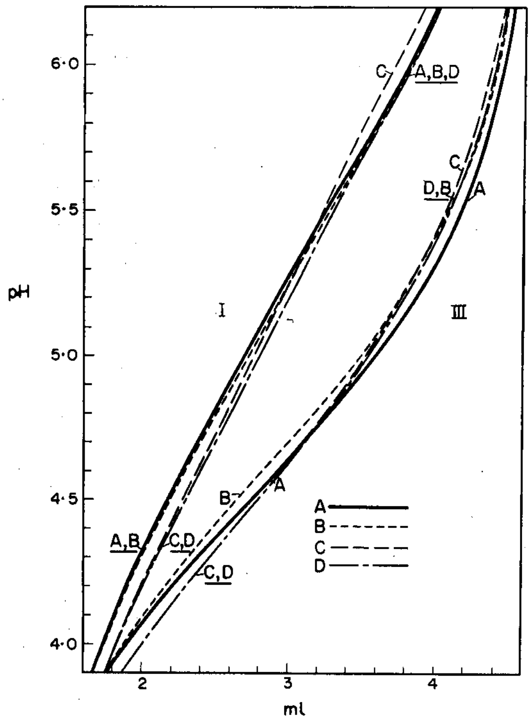

FIG. 2.—The Effect of Variations in Q_{11}, Q_{12} and Q_{13} on the Computed Curves. The roman numerals refer to the experiment number given in the text. The values used in the computation are:

Curve	Q_{11}	Q_{12}	Q_{22}
A	$1{\cdot}0 \times 10^{+8}$	$0{\cdot}70 \times 10^{+13}$	$2{\cdot}0 \times 10^{+15}$
B	$1{\cdot}0 \times 10^{+8}$	$0{\cdot}70 \times 10^{+13}$	$1{\cdot}5 \times 10^{+15}$
C	$1{\cdot}5 \times 10^{+8}$	$0{\cdot}70 \times 10^{+13}$	$2{\cdot}0 \times 10^{+15}$
D	$1{\cdot}5 \times 10^{+8}$	$1{\cdot}4 \times 10^{+13}$	$2{\cdot}0 \times 10^{+15}$

information it is desirable to compute the fractions of each of the species. This can be easily done because (M), (P^-) and (G^-) are known at each point.

The method of obtaining the constants in the present work has the advantages over the iterative procedure used previously[11] in that all of the pertinent data are treated simultaneously and the "best" constants in a "least squares" sense result (see reference 20). Furthermore, by noting the relationships between the experimental conditions and the sensitivities of the curve shapes to the values of the constants, useful information regarding the actual existences of proposed complexes and the proper conditions for studying their properties may be obtained.

SEARCH FOR THE CONSTANTS: A MODIFIED PROGRAMME

The procedure described above is inefficient if all that is desired is the constants for a particular system. The above results indicate that certain modifications in the search procedure can be made to find the minimum more rapidly. The surface $U = F(Q_{11}, Q_{12}, Q_{22})$ is relatively smooth and shows only one important minimum in the region where positive concentrations obtain. Furthermore, in Tables IIA and IIB it is seen that the minimum value of U in each column lies approximately along a downward sloping line which can be drawn across the table. The slope of the line depends on the magnitudes of the increments and the sensitivity of the sum-square to the values of the constants.

To obtain a faster search for the "best" constants the programme has been modified so primarily only those trial sets lying along the valleys shown in Table II are considered. After the preliminary phase where the constants are narrowed down to those giving titration curves falling within some prescribed range, the mapping of the sum-square surface[20] is begun. The value of Q_{11}, at constant Q_{12} and Q_{22}, is incremented until a minimum in U has been reached. This process is then repeated with the next value of Q_{12} but because the valleys slope downward it is not necessary to return Q_{11} to its initial value before starting the new column, but only to reduce it by the value of one increment. As long as the minimum value of U in each new column is found to be smaller than in the preceding column the search at constant Q_{22} continues. Once the lowest value has been reached, ascertained by the simple test that a minimum in a column is larger than that of the preceding column, Q_{22} is increased and Q_{11} and Q_{22} are decreased slightly so as to remain in the vicinity of the minimum.

The search continues in the same manner until the Q_{22} plane having the smallest U has been uncovered. The constants can then be refined either by automatically rescanning the region of minimum U employing smaller and smaller increments until the desired accuracy has been obtained, or by employing procedures based on those described by Hugus[14] or, as illustrated above, Sillén.[20]

Acknowledgement—The author wishes to extend his thanks to the staff of the OSU Numerical Computation Laboratory for their kind assistance and the generous use of their facilities in carrying out this study.

Zusammenfassung—Das Nickel (II)-Pyruvat-Glycinat-System wurde numerisch untersucht. Ein Rechenprogramm zur Lösung der zugehörigen Gleichungen wurde entworfen. Für Bedingungen, die den experimentellen entsprechen, wurden mittels angenommener Konstanten theoretische Titrationskurven berechnet. Die beobachteten Beziehungen zwischen den Werten der Konstanten, den Konzentrantionen der Reaktanten und den sich ergebenden Titrationskurven ergaben wertvolle Informationen über die Bedeutung der verschiedenen gemischten Komplexe unter den verschiedenen Bedingungen. Der "beste" Satz von Konstanten, der gegenüber den experimentellen Daten die kleinste Summe der quadratischen p_H-Abweichungen gibt, wurde erhalten. Die Ergebnisse führen zu einem Verfahren, das auf die Ermittlung der Konstanten in gemischten Komplexsystemen allgemein anwendbar wäre.

Résumé—Une étude quantitative du système Ni(II)-pyruvate-glycinate a été entreprise. On a développé une méthode de résolution des équations correspondantes au moyen d'un calculateur. Les courbes de titrage théoriques correspondant aux conditions expérimentales ont été calculées en utilisant des constantes expérimentales. Les relations observées entre les valeurs des constantes, les concentrations des réactifs, et les courbes de titrage qui en résultent fournissent des renseignements valables concernant l'importance des différents complexes mixtes dans des conditions variées. La "meilleure" série de constantes qui soit en accord avec les données expérimentales est choisie comme étant celle qui donne le minimum pour la somme des carrés des résidus $pH_{calc\ i} - pH_{obs\ i}$. On déduit de ces résultats une méthode qui serait applicable à la détermination des constantes de systèmes de complexes mixtes en général.

REFERENCES

[1] P. Pfeiffer, W. Offerman and H. Werner, *J. prakt. Chem.*, 1941, **159**, 313.

[2] (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1963, **2**, 181; (b) W. Ludwig, *Helv. Chim. Acta*, 1962, **55**, 665.

[3] L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *Proc. Chem. Soc.*, 1962, 255.

[4] (a) P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163; (b) P. E. Figgins and D. H. Busch, *ibid.*, 1960, **82**, 820; (c) M. C. Thompson and D. H. Busch, *ibid.*, 1962, **84**, 1762; (d) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 3016.

[5] D. E. Metzler and E. E. Snell, *J. Amer. Chem. Soc.*, 1952, **74**, 979.

[6] L. David, F. Roddy and D. E. Metzler, *ibid.*, 1961, **83**, 127.

[7] H. N. Christensen, *ibid.*, 1938, **80**, 2305.

[8] H. Mix, *Z. physiol. Chem.*, 1959, **315**, 1.

[9] L. J. Nunez and G. L. Eichhorn, *J. Amer. Chem. Soc.*, 1962, **84**, 901.

[10] (a) T. J. Lane and A. J. Kandathil, *ibid.*, 1961, **83**, 3782; (b) D. F. Martin, G. A. Janusonis and B. B. Martin, *ibid.*, 1961, **83**, 73.

[11] D. L. Leussing, *ibid.*, 1963, **85**, 231.

[12] J. Bjerrum, *Metal-Ammine Formation in Aqueous Solution.* P. Hasse and Son, Copenhagen, 1941.

[13] J. I. Watters, *J. Amer. Chem. Soc.*, 1959, **81**, 1560.

[14] Z. Z. Hugus, *Proceedings of the VIth International Conference on Co-ordination Chemistry.* Macmillan Co., New York, 1961, p. 379.

[15] F. B. Hildebrand, *Introduction to Numerical Analysis.* McGraw-Hill, New York, 1956, p. 447.

[16] Ref. 15, p. 60.

[17] Estimating from the values of the divided differences (ref. 15, p. 147) the error in the interpolation using a second order equation appears to be no more than 0·002 pH unit in the region where the 2nd order approximation is the poorest: the region of negative curvature where the mixed species are beginning to be formed.

[18] P. Zuman, *Coll. Czech. Chem. Comm.*, 1950, **15**, 839.

[19] Inadvertently, the two most acid points shown for curve IV in Fig. 1 had been omitted in the first series of computations. These points were included in the last series. As a matter of interest, exclusion of these points yields a minimum U equal to 0·0175 for which the values of the constants are unchanged.

[20] L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 195; N. Ingri and L. G. Sillén, *ibid.*, 1962, **16**, 173.

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POTENTIOSTATIC DETERMINATION OF KINETIC PARAMETERS OF ELECTRODE REACTIONS WITH GENERATION OF A REACTANT *IN SITU*

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Summary—It is shown that kinetic parameters of simple, fast electrode reactions of the type $O + ne = R$, where R is soluble in the solution or in the mercury electrode, can be determined by the potentiostatic method with a solution initially containing only the substance O, the substance R being generated *in situ* during electrolysis, provided that the electrode reaction involves only a single rate-determining step. Current-time curves are recorded with a fast response, electronic potentiostat and an oscilloscope upon applying a potential step from the zero-current potential to various potentials on the ascending part of the current-potential curve. The forward rate constant k_f at a given potential is calculated from the current at zero time found by extrapolation of the linear portion of the plot of current against square root of time, while the backward rate constant k_b is calculated indirectly from the slope of the same straight line. Plotting log k_f and log k_b against potential allows a simultaneous determination of the formal standard rate constant k_s, both cathodic and anodic transfer coefficients, the number of electrons involved in the rate-determining step and the formal standard potential of the system being studied. This method is considerably simpler than the well-known Gerischer-Vielstich method, and it should be particularly advantageous when R is highly reactive or forms an amalgam which is unstable in air. The upper limit of k_s that can be determined by this method is the same as that determinable by the Gerischer-Vielstich method. The kinetic parameters found by the present method for the electrode reactions zinc ion-zinc amalgam in $1M$ potassium nitrate, copper^{II} ion-copper amalgam in $1M$ potassium nitrate and cadmium ion-cadmium amalgam in $0{\cdot}5M$ sodium sulphate were in fair agreement with the values reported in the literature.

INTRODUCTION

THE potentiostatic method developed by Gerischer and Vielstich[1,2] is a well-established method for the determination of kinetic parameters of fast electrode reactions. In their method, current-time curves are recorded upon applying a potential step from the equilibrium potential of a given system containing initially both oxidised and reduced species at known concentrations, and the exchange current is calculated from the slope at the equilibrium potential of the plot of current at zero time against potential. The standard rate constant and the transfer coefficient are normally

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evaluated by determining the variation of exchange current with the concentration of either oxidised or reduced species. Thus, the Gerischer-Vielstich method suffers experimental complications when the reduced species in solution or in amalgam is highly reactive and subject to air oxidation.

In the method described in this paper, kinetic parameters are evaluated by analysing current-time curves obtained at only one concentration of the oxidised species, the reduced species being absent before electrolysis. Metal ion-amalgam systems can thus be studied by the present method without using an amalgam electrode of accurately known concentration. As expected from theoretical considerations, errors involved in the determination of the backward rate constant are somewhat greater than those involved in the determination of the forward rate constant, particularly at potentials away from the standard potential. Nevertheless, the method should be of practical value, as is evidenced by the fact that the kinetic parameters determined by the proposed method for the few systems are in satisfactory agreement with the values reported in the literature.

CURRENT-TIME RELATIONSHIP

Consider the reduction of a substance O to another substance R in an electrode process involving n electrons at a stationary mercury electrode under the following conditions:

(1) The reduction product R is soluble either in solution or in mercury.
(2) The solution contains the substance O at a known concentration and the concentration of R is negligible before electrolysis.
(3) Because the electrolysis time is very short and the thickness of the diffusion layer is very small in the present potentiostatic method, semi-infinite linear diffusion is the sole mode of mass transfer.
(4) The electrode process involves only a single rate-determining step.
(5) The electrode potential is maintained constant during electrolysis.

The general equation for current-time curves obtained under these conditions is well-known and takes the form[3]

$$i = nFAk_fC_0 \exp(\xi^2)\mathrm{erfc}(\xi) \tag{1}$$

where

$$\xi = \mathrm{s}t^{1/2} \tag{2}$$

$$\mathrm{s} = k_fD_R^{-1/2} + k_bD_R^{-1/2} \tag{3}$$

and i is the current in A, F the Faraday, A the surface area of the electrode in cm^2, k_f and k_b the rate constants for the forward and backward reactions in cm . sec^{-1}, C_0 the concentration of substance O in the bulk of the solution in moles . cm^{-3}, t the time in sec, and D_0 and D_R the diffusion coefficients of 0 and R in cm^2 . sec^{-1}.

For values of ξ smaller than 1, one can write

$$\exp(\xi^2) = 1 + \xi^2 + \frac{\xi^4}{2!} + \ldots$$

and for any values of ξ

$$\mathrm{erfc}(\xi) = 1 - \frac{2}{\sqrt{\pi}}\left(\xi - \frac{\xi^3}{3\cdot 1!} + \ldots\right).$$

When ξ is so small that the higher terms in the above expansion can be neglected, equation (1) can be written in the following form:

$$i = nFAk_fC_0\left(1 - \frac{2s}{\sqrt{\pi}}t^{1/2}\right) \tag{4}$$

This equation predicts that plotting current against $t^{1/2}$ yields a straight line at sufficiently short times at potentials where the condition $st^{1/2} \ll 1$ is fulfilled. The current at $t = 0$ found by extrapolation of this straight line is directly proportional to k_f, while k_b can be calculated from the slope of this line, provided that the diffusion coefficients are known.

On the other hand, k_f and k_b are related to the standard rate constant k_s and potential E by

$$k_f = k_s \exp\left[-\frac{\alpha n_a F}{RT}(E - E^\circ)\right] \tag{5}$$

$$k_b = k_s \exp\left[\frac{\beta n_a F}{RT}(E - E^\circ)\right] \tag{6}$$

where α and β are the cathodic and anodic transfer coefficients and $\alpha + \beta = 1$, n_a is the number of electrons involved in the rate-determining step, and E° is the formal standard potential. Thus, it is anticipated that plotting $\log k_f$ and $\log k_b$ against E should yield two straight lines, and that it should be possible to find k_s and E° from the intersection of these straight lines. From the slopes of these lines, it should be possible to evaluate separately α, β and n_a.

EXPERIMENTAL

Reagents

All chemicals used were of the highest purity available commercially, and they were used without further purification. De-aeration was carried out by passing highly pure tank nitrogen. Solutions of zinc, copper^{II} and cadmium ions were prepared by dissolution of zinc nitrate, copper^{II} nitrate and cadmium sulphate, respectively. The concentrations were determined polarographically in suitable supporting electrolyte solutions.

Apparatus

Electrodes: A dropping mercury electrode with a drop time of about 10 sec was used as the working electrode, and current-time curves were recorded upon closing the circuit at a certain time (8 to 9 sec) after the beginning of the drop formation. The time when the circuit was closed was measured with a stop-watch, and the switch for closing the circuit was operated manually. Current-time curves were perfectly reproducible, indicating that the error resulting from the manual operation of the switch was quite negligible as compared to that associated with the oscilloscopic recording. Because current-time curves were needed only up to 10 msec after the circuit was closed, the variation of surface area of the mercury drop during the recording was also negligible.

A saturated calomel electrode served as the reference electrode, and it was connected with the dropping electrode through a Luggin capillary.

The counter electrode was a platinum foil, which was placed in the compartment separated by a sintered glass disk.

Potentiostat: The potentiostat used in the present study was an electronic potentiostat constructed by the authors according to the circuit designed and described by Shimodaira, Matsuo, Sugawara and Ebiko[4] of this University. The voltage source for 200 V d.c. described in their paper was found to be unsuitable for this type of work and it was replaced by batteries to minimise disturbances resulting from incomplete rectification. The rise time of the potentiostat was about 6×10^{-5} sec, which is one order of magnitude longer than that ($2{\cdot}5 \times 10^{-6}$ sec) of the potentiostat constructed by Electronische Werkstätte of Germany. For the systems studied in this work, however, this was not critical. A micro relay switch was used in the early stages of this investigation. Because this switch generated transients in 0·8 msec, it was later replaced by a sealed-in mercury switch, which was found to give excellent results. The preset potential was read exactly with a potentiometer.

Current-time curves were recorded with a Synchroscope Model SS5151 combined with a high gain differential preamplifier Model SP02-DFH-A, both manufactured by Iwasaki Communication Apparatus Co. Ltd. The calibrated resistances used had a value of 10 to 50 Ω, and the sensitivity of the oscilloscope was always set at the maximum sensitivity of 1 mV. cm^{-1}.

All experiments were carried out in a thermostat maintained at 25°.

RESULTS AND DISCUSSION

Experiments were carried out for reductions of zinc ion in 1*M* potassium nitrate, copper^{II} ion in 1*M* potassium nitrate and cadmium ion in 0·5*M* sodium sulphate. Examples of $i - t^{1/2}$ plots are reproduced in Fig. 1. Good straight lines were obtained in all cases at sufficiently short times. The upper limit of t before which a linear $i - t^{1/2}$ is obtained greatly depends on k_s of the system and also on potential. For example, in the vicinity of the standard potential and for the case of $D_0 = D_R(=D)$, we have $s \approx k_s D^{-1/2}$ [*cf.* equations (3), (5) and (6)]. If one prescribes the condition $st^{1/2} \leq 0{\cdot}2$ for a linear $i - t^{1/2}$ plot to be obtained, then one finds $t \leq 10^{-2}$ sec for a reaction with $k_s = 10^{-3}$ cm.sec^{-1} and $t \leq 10^{-3}$ sec for a reaction with $k_s = 10^{-2}$ cm.sec^{-1}. For faster reactions, current-time curves must be recorded at shorter times. At very short times ($<10^{-4}$ sec), however, correction for the capacity current becomes excessive and limits the maximum measurable value of k_s. The discussion given by

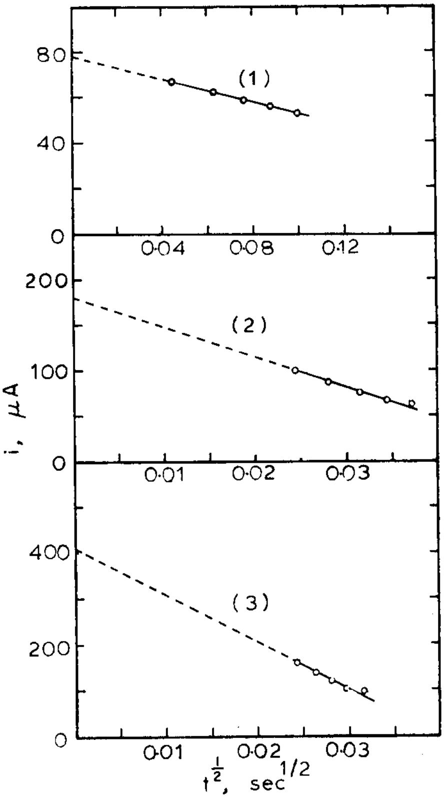

FIG. 1.—Plots of $i - t^{1/2}$: (1) 5 mM Zn^{2+} in 1*M* KNO_3 at −0·986 V; (2) 2 mM Cu^{2+} in 1*M* KNO_3 at +0·034 V; (3) 2 mM Cd^{2+} in 0·5*M* Na_2SO_4 at −0·581 V.

Delahay[5] on this point for the Gerischer-Vielstich method applies directly to the present case, and it can easily be shown that in both methods k_s much greater than 0·2 cm.sec^{-1} cannot be measured. In the experimental examples given in this paper, it was not necessary to measure current at times shorter than 6×10^{-4} sec and the capacity current was quite negligible.

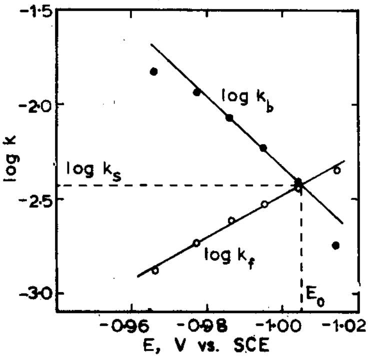

FIG. 2.—Plot of log k − E obtained with 5 mM Zn^{2+} in 1M KNO_3.

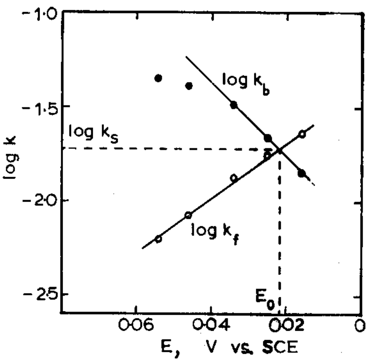

FIG. 3.—Plot of log k − E obtained with 2 mM Cu^{2+} in 1M KNO_3.

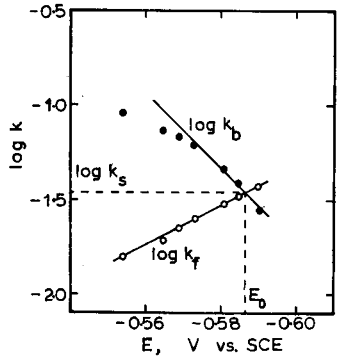

FIG. 4.—Plot of log k − E obtained with 2 mM Cd^{2+} in 0·5M Na_2SO_4.

As is obvious from the theory, a knowledge of diffusion coefficients of both the oxidised and reduced species is required in order to calculate k_b. The values of diffusion coefficients used in the calculation were as follows ($D \times 10^5$ cm^2.sec^{-1}): Zn^{2+} in 1M KNO_3, 0·666; Zn in mercury, 1·57[6]; Cu^{2+} in 1M KNO_3, 0·713[7]; Cu in mercury, 1·06[8]; Cd^{2+} in 0·5M Na_2SO_4, 0·720; Cd in mercury, 2·07[6]. The values for which no literature reference is given were calculated from the average polarographic diffusion current by using the original Ilkovic equation. It is generally recognised that diffusion coefficients calculated in this manner are often in considerable error. For example, the D value of zinc ion calculated by using a modified Ilkovic equation (the numerical constant in the second, correction term being taken equal to 34) was equal to $0·562 \times 10^{-5}$ cm^2.sec^{-1} instead of $0·666 \times 10^{-5}$ cm^2.sec^{-1} found by using the original Ilkovic equation. This difference, however, resulted in only a minor difference in kinetic parameters. For example, the values of k_s for the zinc system calculated with the above two D values were $3{\cdot}6 \times 10^{-3}$ and $3{\cdot}8 \times 10^{-3}$ cm.sec^{-1}, respectively.

Plots of log k_f and log k_b against potential for the three systems studied are shown in Figs. 2, 3 and 4. The kinetic parameters found from these plots are summarised and compared in Table I with the values reported in the literature. In general, the agreement between the values found by the present method and the literature values was satisfactory, except that the k_s value for the copper system was somewhat lower than the value found by other methods.

TABLE I.—KINETIC PARAMETERS AND FORMAL STANDARD POTENTIALS OF SOME METAL ION–AMALGAM SYSTEMS

System	Temp., °C	$E°$, V vs. SCE	k_s, cm.sec^{-1}	n_a	α	β	Method
$Zn^{2+}/Zn(Hg)$ In 1M KNO_3	25	−1·005	$3{\cdot}8 \times 10^{-3}$	2	0·35	0·56	This study
	25		$3{\cdot}5 \times 10^{-3}$				A.C. polarography[9]
$Cu^{2+}/Cu(Hg)$ in 1M KNO_3	25	+0·022	$1{\cdot}9 \times 10^{-2}$	2	0·43	0·53	This study
	25		$4{\cdot}5 \times 10^{-2}$				A.C. polarography[9]
	20		$4{\cdot}5 \times 10^{-2}$				Faradaic impedance[10]
$Cd^{2+}/Cd(Hg)$ in 0·5M Na_2SO_4	25	−0·587	$3{\cdot}6 \times 10^{-2}$	2	0·29	0·62	This study
	25				0·38		A.C. polarography[11]
	25		$2{\cdot}5 \times 10^{-2}$				A.C. polarography[12]
	20		$2{\cdot}6 \times 10^{-2}$		0·25		Voltage-step[13]
	20		$4{\cdot}2 \times 10^{-2}$		0·17		Faradaic impedance[14]
	20		$4{\cdot}5 \times 10^{-2}$		0·22		Current-step[15]

In Figs. 2–4, it is noted that the points for log k_b obtained at less negative potentials tended to deviate in the same direction in all three cases. The reason for this deviation is not obvious. At any rate, it is clear from equation (3) that errors involved in the determination of k_b should be minimum at potentials near the standard potential where k_f and k_b are of the same order of magnitude. It should also be noted that as the potential is made more negative, the current-potential characteristics become steeper and this trend is more marked with faster reactions. At such potentials the precision and stability of potential control of the potentiostat become critical. Also, because current becomes larger at more negative potentials, the effect of iR drop between the working electrode and the tip of the Luggin capillary becomes more serious at more negative potentials. For these reasons, satisfactory k_b values could not be obtained at potentials much more negative than the standard potential. While the present method is simpler than the Gerischer-Vielstich method from the experimental viewpoint, it is the disadvantage of this method that the accuracy in the determination of k_b is less than that in the determination of k_f.

If it is desired that k_b be determined with the same degree of accuracy as k_f in a wider potential range and if the reduced species is sufficiently stable, k_b should be calculated from the anodic current at $t = 0$ measured with a system containing the reduced species alone, the oxidised species being generated *in situ* in this case. It also would be of interest to apply the principle of this method to totally irreversible reactions.

Zusammenfassung—Es wird gezeigt, daß kinetische Parameter einfacher schneller Elektrodenreaktionen vom Typ $O + ne = R$, wo R in der Lösung oder in der quecksilbernen Elektrode löslich ist, mit der potentiostatischen Methode bestimmt werden können. Die Lösung enthält dabei zuerst nur O, R wird *in situ* bei der Elektrolyse erzeugt, vorausgesetzt, daß die Elektrodenreaktion nur einen geschwindigkeitsbestimmenden Schritt enthält. Strom-Zeit-Kurven werden mit einem schnell ansprechenden elektronischen Potentiostaten und einem Oszillographen registriert, wobei das Potential sprunghaft vom Potential, bei dem kein Strom fließt, auf ein Potential im ansteigenden Teil der Stromspannungskurve geändert wird. Die Konstante der Hinreaktion k_f bei einem bestimmten Potential wird aus dem Strom zur Zeit Null berechnet, den man durch Extrapolation des linearen Anstiegs des Stromes gegen die Quadratwurzel der Zeit findet. Die Konstante der Rückreaktion k_b wird indirekt aus der Steigung derselben Geraden berechnet. Trägt man log k_f und log k_b gegen das Potential auf, so erhält man gleichzeitig die formale Standard-Geschwindigkeitskonstante k_s, kathodische und anodische Durchtrittsfaktoren, die am geschwindigkeitsbestimmenden Schritt beteiligte Anzahl von Elektronen und das formale Standardpotential des untersuchten Systems. Diese Methode ist beträchtlich einfacher als die bekannte Gerischer-Vielstich-Methode und sollte besondere Vorteile bieten, wenn R sehr reaktionsfähig ist oder ein nicht luhtbeständiges Amalgam bildet. Das größte bestimmbare k_s ist fier gleich wie bei der Gerischer-Vielstich-Methode. Die nach der neuen Methode gefundenen kinetischen Parameter für die Reaktionen Zinkion-Zinkamalgam in 1m KNO_3, Kupfer(II)-Ion-Kupferamalgam in 1m KNO_3 und Cadmiumion-Cadmiumamalgam in 0,5m Na_2SO_4 stimmten mit den in der Literatur angegebenen Werten befriedigend überein.

Résumé—On montre que les paramètres cinétiques des réactions aux électrodes, simples, rapides et du type $O + ne \rightleftharpoons R$, où R est soluble dans la solution ou dans l'électrode, peuvent être déterminés par une méthode potentiostatique sur une solution qui ne contient initialement que O, la substance R étant fabriquée in situ pendant l'électrolyse. Cette méthode implique qu'une seule réaction détermine la vitesse de la réaction à l'électrode. Les courbes courant-temps sont enregistrées à l'aide d'un potentiostat électronique à réponse rapide et d'un oscilloscope, en appliquant un saut de potentiel allant du potentiel à courant nul jusqu'à divers potentiels de la partie ascendante de la courbe intensité-potentiel. La constante de vitesse directe k_f à un potentiel donné est calculée à partir du courant au temps zéro déterminé par extrapolation de la partie linéaire de la courbe courant-racine carrée du temps, tandis que la constante de vitesse inverse k_b est calculée indirectement à partir de la pente de la même droite. Si l'on trace log k_f et log k_b en fonction du potentiel, on peut déterminer en même temps la constante de vitesse globale k_s, les deux coefficients de transferts cathodique et anodique, le nombre d'électrons mis en jeu au cours de la réaction qui détermine la vitesse, et le potentiel normal du système. Cette méthode est beaucoup plus simple que la méthode bien connue de Gerischer-Vielstich, et devrait être particulièrement avantageuse dans le cas où R est très réactif ou forme un amalgame instable à l'air. La plus forte valeur de k_s que l'on puisse déterminer par cette méthode est la même que celle que l'on détermine par la méthode de Gerischer-Vielstich. Les paramètres cinétiques trouvés par cette méthode pour les réactions à l'électrode: ion zinc-amalgame de zinc dans du nitrate de potassium 1 M, ion cuivre(II)-amalgame de cuivre dans du nitrate de potassium 1 M et ion cadmium-amalgame de cadmium dans du sulfate de sodium 0,5 M sont en bon accord avec les valeurs indiquées dans la littérature.

REFERENCES

[1] H. Gerischer and W. Vielstich, *Z. phys. Chem. (Frankfurt)*, 1955, **3**, 16.
[2] W. Vielstich and H. Gerischer, *ibid.*, 1955, **4**, 10.
[3] P. Delahay, *New Instrumental Methods in Electrochemistry*. Interscience Publishers, New York, N.Y., 1954.
[4] S. Shimodaira, H. Matsuo, G. Sugawara and E. Ebiko, *J. Soc. Metals Japan*, 1962, **26**, 100.
[5] P. Delahay, in *Advances in Electrochemistry and Electrochemical Engineering* edited by P. Delahay. Interscience Publishers, New York, N.Y., 1961. Vol. 1, p. 254.
[6] A. G. Stromberg, *Doklady Akad. Nauk. S.S.S.R.*, 1952, **85**, 831; *Chem. Abs.*, 1953, **47**, 51.
[7] L. Meites, *Polarographic Techniques*. Interscience Publishers, New York, N.Y., 1955.
[8] N. H. Furman and W. C. Cooper, *J. Amer. Chem. Soc.*, 1950, **72**, 5667.
[9] T. Kambara and T. Ishii, *Rev. Polarography*, 1961, **9**, 30.
[10] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, 1952, **48**, 951.
[11] H. H. Bauer and P. J. Elving, *Analyt. Chem.*, 1958, **30**, 341.
[12] H. H. Bauer, D. L. Smith and P. J. Elving, *J. Amer. Chem. Soc.*, 1960, **82**, 2094.
[13] W. Vielstich and P. Delahay, *ibid.*, 1957, **79**, 1874.
[14] H. Gerischer, *Z. Elektrochem.*, 1953, **57**, 605.
[15] T. Berzins and P. Delahay, *J. Amer. Chem. Soc.*, 1955, **77**, 6448.

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THE BORON-CARBON-HYDROGEN SYSTEM

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Summary—Identification of many newly-discovered compounds composed only of the three elements, B, C and H, has been accomplished by use of mass, infrared and nuclear magnetic resonance spectroscopy in conjunction with the isotopic substitution technique. These compounds can be classified into two general categories: (1) the organo derivatives of boron hydrides, and (2) the carboranes (and their organo derivatives). Examples of compounds identified by purely spectroscopic means are given.

THE state of the art of the B-C-H system as of 1942 has been summarised by Schlesinger and Burg.[1] Actually, in addition to the trialkyl boranes, only the alkyldiboranes were prepared and some of their physical properties given. Very little progress in this area was made until 1952, when the present author introduced the isotopic boron technique with spectroscopy as a routine analytical tool for identification of boron-containing compounds. Since that time the organo-substitution compounds of the higher boron hydrides, as well as new boron-carbon systems, have been prepared and identified. It is the purpose of this paper to discuss the various ramifications of these analyses with respect to the identification of the new organoboron compounds.

ANALYTICAL TECHNIQUES

Mass spectrometry

In boron chemistry the mass spectrometer is a particularly useful tool because of the readiness with which compounds of varying isotopic boron composition may be prepared. Isotopically-normal and ^{10}B-enriched organoboranes of the same chemical composition can be prepared by the reaction of unsaturated organic compounds or alkyl halides with corresponding isotopically-normal or ^{10}B-enriched boron hydrides. The exact number of boron atoms in the organoboranes can then be calculated from the shift in peak heights of their mass spectra. The number of carbon and hydrogen atoms can be obtained from the difference of the molecular weight (corresponding to the highest *m/e* value) and the accountable mass of the boron atoms. No shift in corresponding mass spectra distinguishes pure organic compounds from those containing boron. As an extension of this technique, deuterated compounds can be used to verify the number of hydrogen atoms attached to the carbon and/or boron atoms.

As a matter of historical importance, the discovery (1953) of the carborane series of compounds was a direct application of this isotopic boron technique coupled with mass spectroscopy. Fig. 1 shows the comparison of the mass spectra of products formed by the reaction of acetylene with ^{10}B-enriched and isotopically-normal diboranes. In this case, no fractionation of products was made; consequently, the mass spectra represent a composite spectra of all components in the mixture. A high peak at *m/e* 78 in both spectra must belong to a pure organic compound; subsequent purification and analysis indicated that this pronounced peak at *m/e* 78 is produced by benzene. The general contour of the three distinct groups of peaks in the high mass range indicates polyboron-containing compounds. This "boron shape" is a function of the number of boron atoms and the isotopic composition.[2] For example, the high peak at *m/e* 95 in the ^{10}B-spectrum shifts to *m/e* 100 in the normal spectrum; the shift of 5 units indicates a B_5-compound. Similarly, the shift from *m/e* 109 to *m/e* 114 also indicates a B_5-compound, and the shift from *m/e* 114 to *m/e* 122 signifies a B_8-compound. All of these compounds were later isolated and identified as belonging to the carborane series.

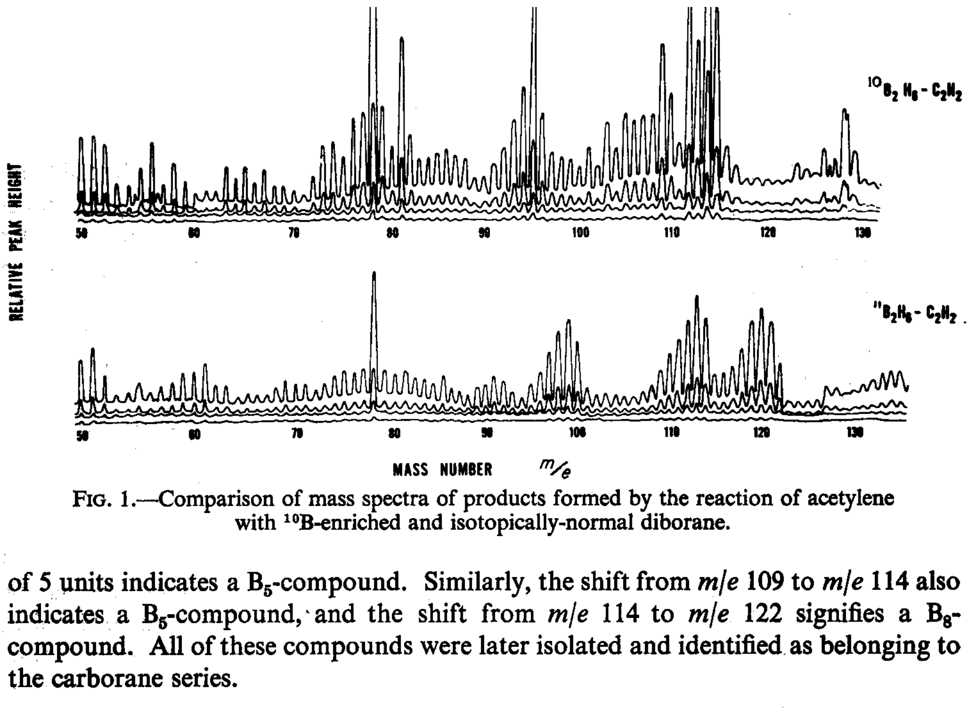


FIG. 1.—Comparison of mass spectra of products formed by the reaction of acetylene with ^{10}B-enriched and isotopically-normal diborane.

Infrared spectroscopy

Infrared spectral analysis gives an insight into group arrangements of boron, carbon and hydrogen in the compounds. It is possible, for example, to distinguish between terminal borons (B_t-H) and bridge borons (B-H-B), such as those illustrated in Fig. 2, which shows the absorption peaks for the alkyl diboranes.[3] The bridge-boron absorption frequency is in the 1600 cm^{-1} range; and the terminal boron frequency in the 2500 cm^{-1} range. Further, it is possible to distinguish the number of hydrogen atoms attached to the terminal boron—a single peak indicates one hydrogen and a double peak indicates two hydrogens.

The shift in absorption frequency upon partial deuteration of the organoboron compound can be used to locate the position of the hydrogen (deuterium), *i.e.*, whether it is attached to the boron atom or to the carbon atom.

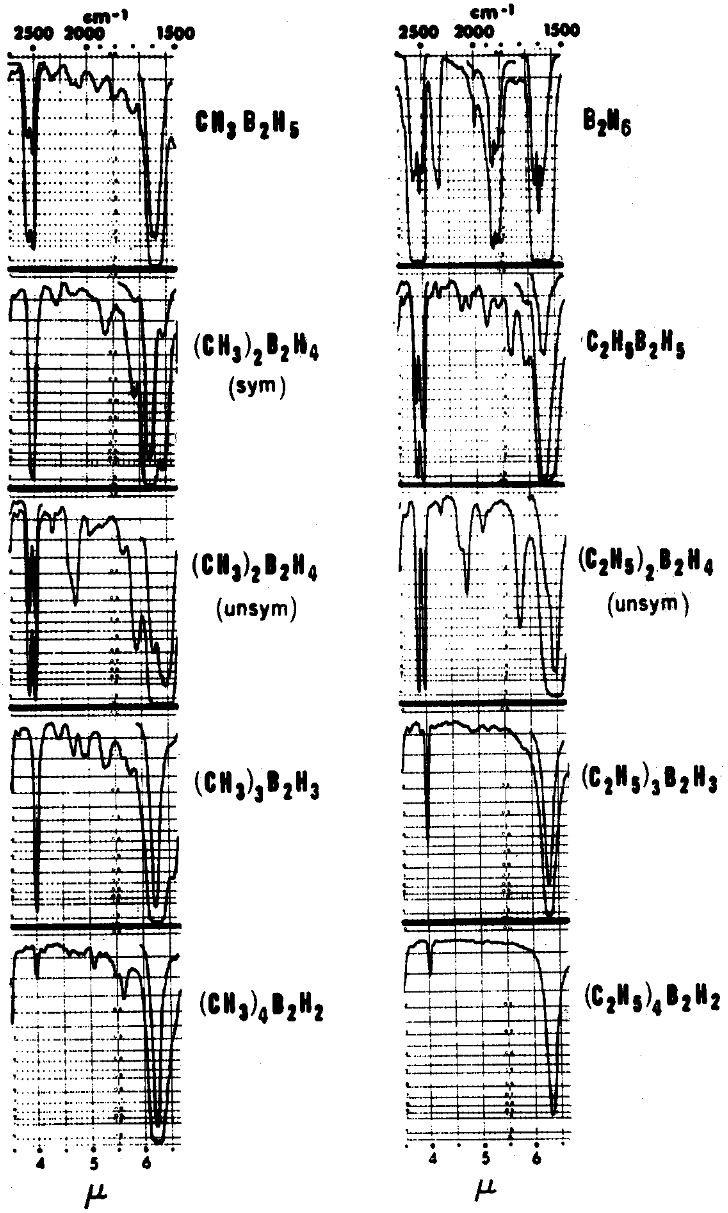


FIG. 2.—Infrared region 1500–2850 cm^{-1} showing terminal hydrogen and bridge hydrogen absorptions in alkyldiboranes.

Nuclear magnetic resonance spectroscopy

For complete analysis of organoboron compounds, one should be able to derive the structure of the compound so that one can locate the actual position of, say, an alkyl group, substituted for a hydrogen atom. For example, for a monoalkyl pentaborane, one would like to know whether the alkyl group is located at an apex boron position or on a base boron position. Such information is not readily available from either mass or infrared spectral analyses. By n.m.r. spectroscopy, one can easily distinguish between such positions.

The ^{11}B n.m.r. spectrum yields information of the environment of the boron nucleus. The interaction of a single proton with boron results in a doublet, whereas a BH_2 unit will be represented by a triplet. On the other hand, a boron atom without hydrogen attached will be represented by a singlet. Bridge hydrogens are not observed. Replacement of deuterium for hydrogen collapses the doublet or triplet to a singlet. Because of chemical shift, borons in different positions also can be distinguished. The n.m.r. spectra of the various boron hydrides have been summarised, both by splitting and chemical shift.[4] Alkyl substitution on boron hydrides will manifest itself both by changes in number of peaks and/or relative position in the spectra. Examples of such changes will be given later.

In the proton n.m.r. spectrum, the interaction of the ^{11}B nuclear spin of 3/2 with a proton results in a quartet of (equal size) peaks. On the other hand, the C-H interaction is a single peak. Bridge hydrogens (B-H-B) are manifested by a broad unresolved peak. Because the proton spectrum is the sum of all component peaks, the proton spectrum may at first appear complicated; however, in most instances the spectrum can be reconciled with the structure of the compound, and thus serve as a verification of structure.

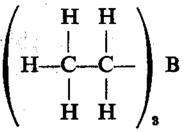
ORGANOBORON COMPOUNDS—COMPOSITION AND STRUCTURE

The organoboron compounds (containing only B, C and H) fall into two general categories: (1) Derivatives of boron hydrides, and (2) carboranes. In the first category, the organic component (alkyl, aryl, *etc.*) usually is appended to a boron hydride, whereas the term "carborane" was coined to signify that the carbon atom had become an integral part of the boron skeleton. Organo derivatives of carboranes also have been synthesised. In this instance the organic component is appended either to a boron or carbon atom in the carborane. Thus, the number of possible organoboron compounds is large, and new compounds are constantly being discovered. It is apparent that simple elemental analysis no longer suffices in identifying these compounds.

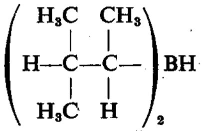
Derivatives of boron hydrides

1. *Monoborane:* The trialkylboranes (BR_3) are well known, and can be prepared by the Grignard reaction or by the addition of diborane to alkenes. If the alkene is a low molecular weight compound, *e.g.*, ethylene, the product will be triethylborane; or in the case of excess diborane, the various ethyl diboranes.

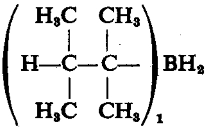
Interestingly, it is not possible to form BHR_2 or BH_2R in the simple compounds because of the great tendency of the boron to be tetrahedrally bonded, thus resulting in dimerisation. However, if the alkene is complex so as to present a large steric hindrance, the monoborane containing one or two hydrogens can be formed,[5] *viz.*,



$\left(\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}}\right)_3\mathrm{B}$



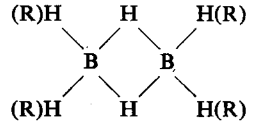
$\left(\mathrm{H{-}\overset{H_3C}{\underset{H_3C}{C}}{-}\overset{CH_3}{\underset{H}{C}}{-}}\right)_2\mathrm{BH}$



$\left(\mathrm{H{-}\overset{H_3C}{\underset{H_3C}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}}\right)_1\mathrm{BH_2}$

The alkenylboranes, alicyclic boranes and triarylboranes also are known.

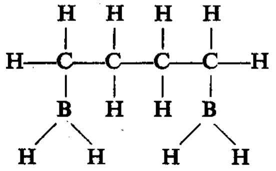
2. *Diborane:* The alkyl diboranes have the same basic boron structure as diborane, *viz.*, two boron atoms held together by two bridge hydrogens with substitution occurring at any of the four terminal hydrogens:

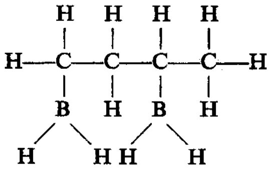


The five possible substituted simple alkyldiboranes had been prepared as early as 1935;[7] however, the purity of some of these compounds may be questionable because of the equilibrium which exists between the various alkyldiboranes. It was not until the advent of spectroscopy that the purity of these compounds could be monitored with any degree of accuracy.[8]

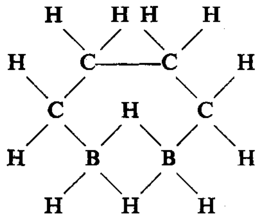
That the molecule contains two boron atoms can be recognised by mass spectral analysis of isotopic variants of the compounds.[9] Infrared analyses[3,8] reveal the presence of B-H-B bridge bonds. The R groups attached to the borons are restricted to low molecular weights; with large sterically hindered groups the molecule dissociates to BH_2R or BHR_2, as mentioned previously.

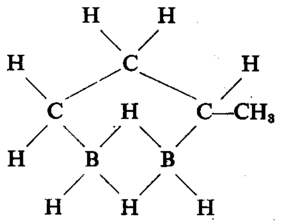
The addition of diborane to alkenes has been studied extensively by H. C. Brown and his school. In the case of the addition of diborane to 1,3-butadiene, Brown[10] reports two possible structures to yield polymeric products:





The reaction of diborane with 1,3-butadiene under different experimental conditions also was carried out in the present author's laboratory.[11] In addition to polymeric products, the product contained an appreciable amount of the 1:1 butadiene diborane addition product. Spectroscopic analyses (mass, infrared and n.m.r.) clearly show two cyclic compounds as follows:

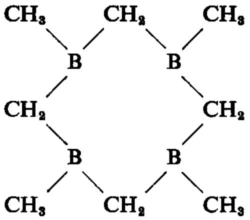




Apparently the presence of two BH_2 groups in the same compound results in tetrahedral boron bond formation. The equivalence of the four hydridic hydrogens (attached to boron) was shown by complete exchange of these hydrogens with deuterium of deuteriodiborane. Such exchanges occur freely in diborane. Interestingly, deuterium in B_2D_6 does not exchange with hydrogen attached to carbon, thus this exchange technique is useful in determining the number of hydrogens attached to boron.[11]

3. *Tetraborane:* To date, there is only one organotetraborane known. This compound formed by the reaction of ethylene with tetraborane has been identified as 2,4-dimethylenetetraborane.[12,13] That the ethylene molecule adds across the 2,4 boron sites is evident in the infrared spectrum by the change of the doublet (BH_2) to a singlet (BH) for the B-H terminal stretching absorption peak. The ^{11}B n.m.r. spectrum confirms this conclusion in that the low field triplet (BH_2) of tetraborane changes to a doublet (B-H), whereas the high field doublet remains unchanged (boron sites 1,3) (see Fig. 3).

In the thermal decomposition of trimethylborane, Goubeau[14] reports the formation of a compound containing four boron atoms [$(BCH_2)_4(CH_3)_4$]; however, this compound is visualised as four boron atoms and four CH_2 groups connected alternatively in a ring with a methyl group attached to each boron atom, *viz.*,



Although this compound contains four boron atoms, this compound obviously does not qualify as a tetraborane, but rather as a monoborane.

4. *Pentaborane:* Alkyl pentaboranes have been formed in our laboratory by a number of methods, *viz.*, reaction of pentaborane with ethylene or with alkyl halides and aluminum chloride, or by the Grignard reaction. Identification of the various alkylated pentaboranes was made by mass spectral analysis.

Extensive studies on the alkylated pentaboranes also have been carried out at the Explosives Research and Development Establishment in England.[15,16] The various alkylated pentaboranes were separated by gas chromatography and identified by n.m.r. spectroscopy. Up to five ethyl groups have been substituted on pentaborane. Because pentaborane consists of four equivalent boron atoms in a base and one atom in the apex of a tetragonal pyramid, the substitution of alkyl groups gives rise to isomers, and such isomers can be identified by n.m.r. spectra. For monoethylpentaborane the ethyl group can be apex or base substituted and its location can be determined by whether the apex doublet or base doublet of pentaborane collapses to a singlet. Diethylpentaborane and tetraethylpentaborane also can have only two isomers, but triethylpentaborane has three possible isomers. All of the possible isomers of the ethylated pentaboranes have been observed.[16]

5. *Decaborane:* Alkyldecaboranes can be formed by analogous reactions of the alkylpentaboranes. The mass spectrum of monoethyldecaborane already has been given.[17] The various isomers of the alkyldecaboranes can be identified by the changes in the n.m.r. spectrum of decaborane.[18]

The following methyldecaboranes have been prepared and analysed:[19–21] 2-, 5- and 6-methyl-; 1,2-, 2,4-, 5,6- and 6,9-dimethyl-; 1,2,3- and 1,2,4-trimethyl-; 1,2,3,4- and 1,2,3,5-tetramethyldecaborane. For the ethyldecaboranes the following derivatives have been prepared:[16,20,22] 1-, 2-, 5- and 6-ethyl-; 1,2- and 2,4-diethyl; at least three isomers of triethyl-, and at least three isomers of tetra-ethyldecaboranes. Benzyldecaborane also has been reported.[23]

6. *Other boron hydrides:* Although not yet reported, organoderivatives of other boron hydrides, such as hexaborane, octaborane, nonaborane, and higher boron hydrides, are anticipated.

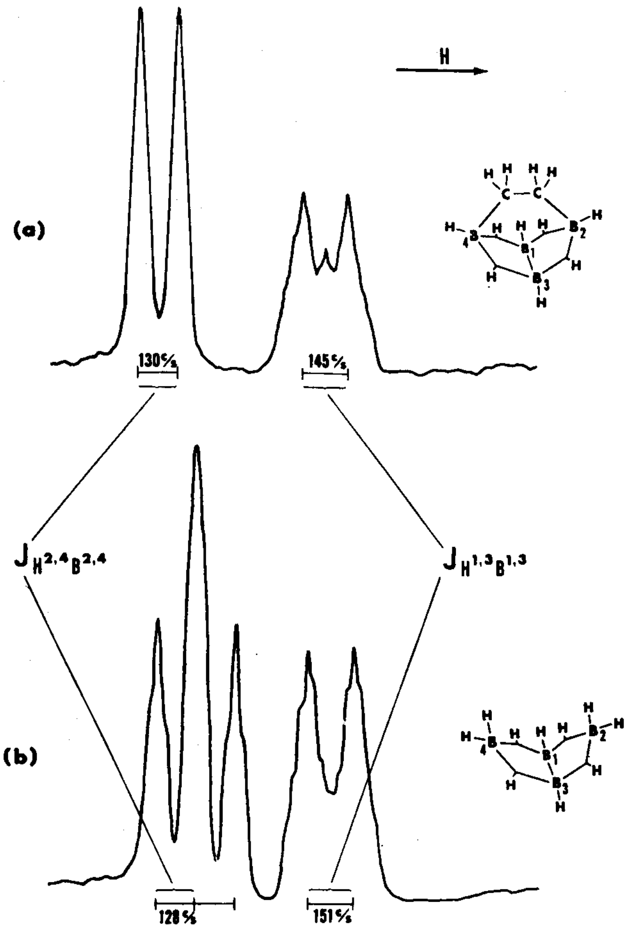


FIG. 3.—Comparison of ^{11}B n.m.r. spectra of tetraborane and 2,4-dimethylenetetraborane.

Carboranes

As mentioned previously under the section on *Mass spectrometry*, the study of the reactions of acetylene with various boron hydrides led to the discovery of a new class of organoboron compounds. From spectroscopic identification and characterisation of these compounds, it was shown that they differed from other known boron-carbon compounds. These new compounds have no bridge hydrogens and the carbon atoms are incorporated into the structure of the boron network; consequently, these compounds were named "carboranes". The generic formula for this series of compounds is $B_nC_2H_{n+2}$.[24] Although the entire series of carboranes can be formed by the low pressure flashing reaction of diborane and acetylene, better yields can be obtained by use of the higher boron hydrides as discussed below.

1. *Carborane*-3 ($B_3C_2H_5$): This compound was one of a series of carboranes prepared by the reaction of pentaborane and acetylene in the silent discharge apparatus.[24] Identification was made by comparison of the mass spectra of isotopic variants of the compound, *viz*., $^{10}B_3C_2H_5$, $B_3C_2H_5$, $B_3C_2H_3D_2$, $B_3C_2D_3H_2$ and $B_3C_2D_5$. From infrared and n.m.r. spectra, the structure of the compound is regarded as a trigonal bipyramid with the three boron atoms in one plane and one carbon above and below the boron plane. The hydrogens attached to the boron and carbon atoms are the same as originally present in the parent compound. The deuterium in deuteriodiborane will exchange with the hydrogens attached to the boron atoms, but not with the hydrogens attached to the carbons. This selectivity of hydrogen-deuterium exchange is common to the boron hydrides and is the basis of a method for determining the location of hydrogen, *i.e*., whether attached to boron or carbon atoms.

2. *Carborane*-4 ($B_4C_2H_6$): Two isomers of carborane-4 have been identified.[25] The symmetrical isomer is analogous to $B_3C_2H_5$, except that there are four borons in one plane; in the unsymmetrical form, one carbon and one boron atom have interchanged positions. Because of similarities in the vapour pressures of carborane-4 and pentaborane (parent compound), it is not possible to separate the two compounds by direct fractional distillation. However, such separation can be effected by first complexing the pentaborane with triethylamine to change the degree of volatility. The excess triethylamine can be complexed with diborane.

3. *Carborane*-5 ($B_5C_2H_7$): This compound has been identified by comparison of the mass spectra of the ^{10}B-enriched and isotopically-normal variants of the compound.[26] One characteristic feature of the carboranes is the low degree of skeletal breakdown observed in their fragmentation patterns.

4. *Carborane*-8 ($B_8C_2H_{10}$): This compound also has been identified by application of the isotopic boron technique and mass spectrometry.[26] In addition to use of pentaborane as a parent compound, carborane-8 is a product when acetylene is reacted with tetraborane or decaborane.

5. *Carborane*-10 ($B_{10}C_2H_{12}$): Carborane-10 can be prepared conveniently by the reaction of acetylene with decaborane.[26] The n.m.r. spectra of carborane-10 is consistent with the concept that the two carbon atoms replace the four bridge hydrogens of decaborane,[18] thus completing the icosahedron structure.* This compound is quite stable.

6. *Alkyl derivatives of carboranes:* In the preparation of the carboranes from acetylene, it has been observed that various alkylated derivatives of the different carboranes are also formed. The alkylated derivatives of the carboranes are also formed by reaction of boron hydrides with alkylated acetylenes, *e.g*., methylacetylene. The derivatives observed in the mass spectra are as follows: $B_3C_3H_7$, $B_3C_4H_9$, $B_4C_3H_8$, $B_4C_4H_{10}$, $B_5C_3H_9$, $B_5C_4H_{11}$, $B_5C_5H_{13}$, $B_5C_6H_{15}$, $B_8C_3H_{12}$ and $B_8C_4H_{14}$. Numerous derivatives of $B_{10}C_2H_{12}$ also have been formed; these compounds will be the subject of a separate paper.

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* The introduction of the two boron atoms of diborane into the decaborane structure results in the unstable $B_{12}H_{12}$ molecule;[27] however, the $B_{12}H_{12}^{-2}$ ion is reported to be stable with an icosahedral arrangement.[28]

Dihydrocarborane

When pentaborane and acetylene react at low pressures, carborane-4 is formed; however, when these same reactants are confined under pressure at elevated temperatures, the product is another organoboron compound whose composition is $B_4C_2H_8$.

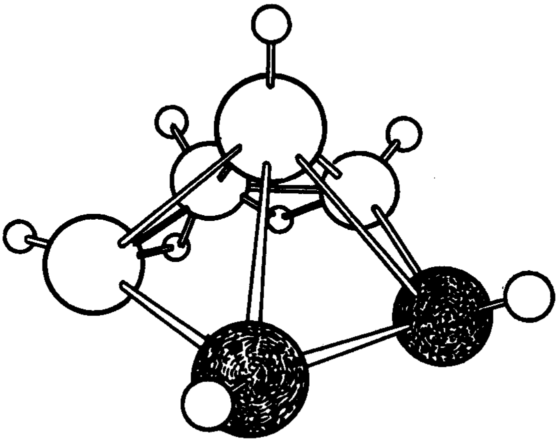

FIG. 4.—Structure of dihydrocarborane-4 ($B_4C_2H_8$).

Before being analysed by n.m.r. spectroscopy, this compound was believed to be "ethenyltetraborane";[29] however, subsequent studies in our laboratory indicate that the compound is structurally similar to hexaborane-10 in which the two carbon atoms have replaced two boron atoms and two bridge hydrogens in the base of the pentagonal pyramid (Fig. 4). Consequently, this compound is named "dihydrocarborane-4". Recently,[30] some alkyl derivatives of $B_4C_2H_8$ have been reported.* It is very probable that other dihydrocarboranes will be prepared in the future.

Now that pure organoboron compounds can be synthesised and identified, methods for elemental analysis of boron and carbon are being developed.[31,32]

Zusammenfassung—Die Identifizierung vieler neuentdeckter Verbindungen, die nur die Elemente B, C und H enthalten, gelang mittels Massen-, Infrarot- und Kernresonanzspektroskopie in Verbindung mit Isotopensubstitution. Die Verbindungen können in zwei Klassen aufgeteilt werden: 1) organische Derivate der Borhydride und 2) Carborane (und ihre organischen Derivate). Beispiele von Verbindungen, die mit ausschließlich spektroskopischen Mitteln identifiziert wurden, werden angegeben.

Résumé—L'identification de nombreux composés nouvellement découverts, constitués seulement par les trois éléments B, C et H, a été réalisée par l'emploi des spectroscopies de masse, infrarouge, et de résonance magnétique nucléaire, en liaison avec la technique de substitution isotopique. Ces composés peuvent être classés en deux catégories générales: (1) les organo-dérivés des borohydrures et (2) les "carboranes" (et leurs dérivés organiques). On donne des exemples de composés identifiés par des méthodes purement spectroscopiques.

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* Attention is called to the fact that the structure of $B_4C_2H_8$ cited recently[30] was taken from the work of I. Shapiro and H. G. Weiss without permission or acknowledgment of the senior investigator.

REFERENCES

[1] H. I. Schlesinger and A. B. Burg, *Chem. Rev.* 1942, **31,** 1.

[2] I. Shapiro, C. O. Wilson, J. F. Ditter and W. J. Lehmann, *Adv. in Chem. Series*, 1961, **32,** 127.

[3] I. Shapiro, C. O. Wilson and W. J. Lehmann, *J. Chem. Phys.*, 1958, **29,** 237.

[4] R. E. Williams, S. G. Gibbins and I. Shapiro, *J. Amer. Chem. Soc.*, 1959, **81,** 6164.

[5] H. C. Brown and A. W. Moerikoper, *ibid.*, 1962, **84,** 1478.

[6] G. E. Coates, *Organo-Metallic Compounds.* John Wiley and Sons, New York, 1960, p. 88 and refs. therein.

[7] H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, 1935, **57,** 621.

[8] W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, 1961, **17,** 396.

[9] C. O. Wilson and I. Shapiro, *Analyt. Chem.*, 1960, **32,** 78.

[10] G. Zweifel, K. Nagase and H. C. Brown, *J. Amer. Chem. Soc.*, 1962, **84,** 183.

[11] H. G. Weiss, W. J. Lehmann and I. Shapiro, *ibid.*, 1962, **84,** 3840.

[12] B. C. Harrison, I. J. Solomon, R. D. Hites and M. J. Klein, *J. Inorg. Nuclear Chem.*, 1960, **14,** 195.

[13] I. Shapiro, R. E. Williams and S. G. Gibbins, *J. Phys. Chem.*, 1961, **65,** 1061.

[14] J. Goubeau and R. Epple, *Ber.*, 1957, **90,** 171.

[15] B. Figgis and R. L. Williams, *Spectrochim. Acta*, 1959, **15,** 331.

[16] N. J. Blay, J. Williams and R. L. Williams, *J. Chem. Soc.*, 1960, 424.

[17] A. Quayle, *J. Appl. Chem.*, 1959, **9,** 395.

[18] I. Shapiro, M. Lustig and R. E. Williams, *J. Amer. Chem. Soc.*, 1959, **81,** 838.

[19] R. L. Williams, I. Dunstan and N. J. Blay, *J. Chem. Soc.*, 1960, 5006.

[20] I. Dunstan, N. J. Blay and R. L. Williams, *ibid.*, 1960, 5016.

[21] I. Dunstan, R. L. Williams and N. J. Blay, *ibid.*, 1960, 5012.

[22] N. J. Blay, I. Dunstan and R. L. Williams, *ibid.*, 1960, 430.

[23] B. Siegel, J. Mack, J. Lowe and J. Gallaghan, *J. Amer. Chem. Soc.*, 1958, **80,** 4523.

[24] I. Shapiro, C. D. Good and R. E. Williams, *ibid.*, 1962, **84,** 3837.

[25] I. Shapiro, B. Keilin, R. E. Williams and C. D. Good, *ibid.*, 1963, **85,** 3167.

[26] I. Shapiro, presented at the XIX International Congress for Pure and Applied Chemistry, London, July, 1963.

[27] I. Shapiro and R. E. Williams, *ibid.*, 1959, **81,** 4787.

[28] J. A. Wunderlich and W. N. Lipscomb, *ibid.*, 1960, **82,** 4427.

[29] I. Shapiro and H. G. Weiss, *U.S. Patent* 3, 086, 996 (Apr. 23, 1963), filed June 13, 1956.

[30] T. P. Onak, R. E. Williams and H. G. Weiss, *J. Amer. Chem. Soc.*, 1962, **84,** 2830.

[31] I. Dunstan and J. V. Griffiths, *Analyt. Chem.*, 1961, **33,** 1598.

[32] R. H. Pierson, *ibid.*, 1962, **34,** 1642.

Talanta, 1964, Vol. 11, pp. 221 to 229. Pergamon Press Ltd. Printed in Northern Ireland

POLAROGRAPHIC REDUCTION OF MANGANESE^{III} IN AN ALKALINE TARTRATE SOLUTION

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Summary—The formation of manganese^{III} complexes by the air oxidation of manganese^{II} in alkaline tartrate solution is confirmed by measurement of the direct current and the Kalousek polarograms. A distinct minimum is observed on the polarogram in the pH range from 10 to 13. The effects of pH, the concentration of sodium tartrate and surface-active substances on the polarogram are investigated, and the electrode processes of manganese^{III} in an alkaline tartrate solution are discussed.

THE polarographic reduction of manganese^{II} has been extensively studied, but that of manganese^{III} has not received full investigation. Kolthoff and Watters[1] studied the reduction of the pyrophosphate complex of manganese^{III}, which was prepared by the preliminary oxidation of manganese^{II} in a pyrophosphate solution with excess lead dioxide. Novák, Kůta and Říha[2] studied the polarographic behaviour of manganese^{III} in a solution containing sodium chloride, sodium hydroxide and triethanolamine. Svátek, Roubal and Přibil[3] found a reversible wave for the manganese^{III} complex with pyrocatechol-3,5-disulphonate in an ammoniacal buffer and in sodium hydroxide solution. Verdier[4] reported the polarographic reduction of hexacyanomanganate$^{(III)}$, which was prepared by air oxidation of manganese^{II} in potassium cyanide solution. He[4] found, however, that in 2*M* potassium hydroxide solution containing sodium tartrate, manganese^{II} was oxidised to manganese^{IV} by atmospheric oxygen.

The present paper is concerned with a polarographic study of the manganese^{III} complex produced by the air oxidation of manganese^{II} in an alkaline tartrate solution. The oxidation state of the complex is discussed on the basis of the direct current and the Kalousek polarograms obtained. The minimum on the current-voltage curve is explained from the standpoint of the charges of the complex and the electrode. The deceleration and the acceleration of the electron-transfer process by the addition of surface-active ions are demonstrated.

EXPERIMENTAL

The manganese^{III} was prepared by air oxidation of manganese^{II} in an alkaline tartrate solution. The formation of manganese^{III} was confirmed by the polarographic method described later. A 0·1*M* manganese^{II} solution was prepared by dissolving a known amount of manganese^{II} chloride tetrahydrate.

Direct current (d.c.) polarograms were recorded by a Yanagimoto PB-4 pen-recording polarograph and a Yanagimoto Galvarecorder GR-103 with an automatic potential scanner. A Yanagimoto Galvarecorder Y-GR 2 with an automatic potential scanner was used to record alternating current (a.c.) polarograms. Kalousek polarograms[5] were obtained with the same circuit as previously described.[6,7] Current-time (i-t) curves were recorded using a Rikadenki ER-J 1 recorder with an RLDC-201 preamplifier. An electrolysis cell of a simple beaker type was used in all measurements. The dropping mercury electrode (DME) used had an m value of 2·16 mg/sec and a drop time t_d of 4·59 sec, being measured in 0·1*M* potassium chloride solution containing 0·005% of gelatin at 25°

and −0·5 V *vs.* SCE at a 40 cm height of the mercury reservoir. The potential of the DME was measured against a saturated calomel electrode (SCE), which was connected to the electrolytic solution through a Hume and Harris type salt bridge. When a.c. polarograms were measured, a platinum wire electrode of a large surface area was inserted in the electrolytic solution as the third electrode, which was terminated at the SCE through a 100-μF capacitor. A Hitachi Model EHP-1 pH meter was used for measurement of the pH of the solution.

All measurements were carried out in a thermostat of 25° ± 0·1°, and the dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. Precautions were taken against oxygen and light for manganese^{II} and manganese^{III}* solutions, respectively. The d.c. and Kalousek polarograms given in this paper are corrected for the residual current.

RESULTS AND DISCUSSION

Manganese species in an alkaline tartrate solution

Polarograms of 1·2 mM of manganese obtained before and after the air oxidation in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and 0·005% of gelatin are reproduced in Fig. 1. The polarogram of manganese^{II} (curve 1) is the same as that reported by Er-Kong and Vlček.[8] They consider that manganese^{II} exists in various forms of mono- and binuclear hydroxotartratomanganate$^{(II)}$, of which only the mononuclear complexes are reducible at the dropping mercury electrode. The polarogram obtained after the air oxidation (curve 2) shows a remarkable minimum, and does not coincide with the polarogram obtained by Verdier[4] in 2*M* potassium hydroxide solution containing sodium tartrate. The limiting currents of curve 2 measured at −1·55 V and −1·90 V were both proportional

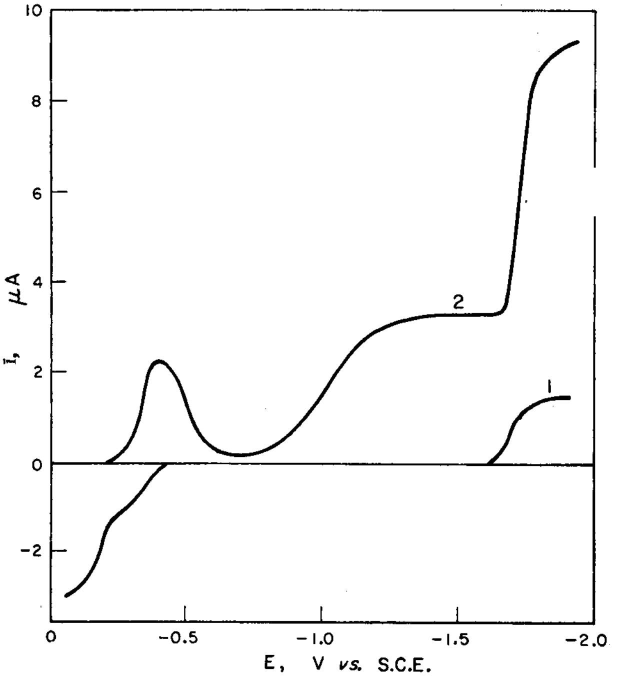

FIG. 1.—Polarograms of 1·2 mM of manganese in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and 0·005 % of gelatin, obtained before (curve 1) and after (curve 2) the air oxidation.

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* Photochemical reduction of manganese^{III} in an alkaline tartrate solution is reported elsewhere.

to the concentration of manganese^{II} added, and the ratio of the latter to the former was found to be 2·96 after correction for the drop time. This means that the limiting current at −1·55 V is from the one-electron reduction of manganese^{III} to manganese^{II} because the second wave starting approximately at −1·6 V is a reduction wave of manganese^{II} to manganese^{0}.

The formation of manganese^{III} was also confirmed by the Kalousek polarograms recorded before and after the air oxidation. Curves 1 and 2 in Fig. 2 are the Kalousek polarograms which were recorded with an alkaline tartrate solution of manganese^{II} at −0·10 V and −0·30 V of E_2 potential.[6,7] The cathodic part of the polarograms is essentially the same as the polarogram obtained after the air oxidation. The Kalousek polarograms recorded after the air oxidation (curves 3 and 4 in Fig. 2) give anodic waves, which are similar to those observed with the alkaline tartrate solution of manganese^{II}. These observations suggest that the product obtained by the air oxidation is the same as that obtained by electro-oxidation. In addition, the Kalousek polarograms of the alkaline tartrate solution of manganese^{III} recorded at −0·42 V and −1·55 V of E_2 potential show that the reduction products are the same at both potentials and that the potential of the anodic wave agrees with that of the mononuclear manganese^{II} tartrate complexes.[8] This suggests that the manganese^{III}-tartrate complex obtained by the air oxidation is of a mononuclear type.

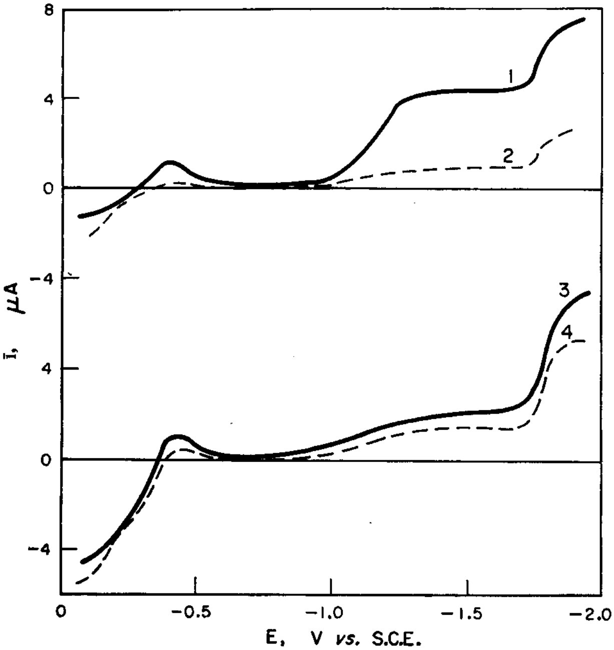

FIG. 2.—Kalousek polarograms of 1·2 mM of manganese^{II} (curves 1 and 2) and manganese^{III} (curves 3 and 4) in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and gelatin (0·005 % for 1 and 2 and 0·001 % for 3 and 4). E_2 potentials are:

(1) −0·10 V; (2) −0·30 V; (3) −0·42 V; (4) −1·55 V *vs.* SCE.

Effect of pH, tartrate concentration and potassium nitrate

A synoptical denotation of the wave is given in Fig. 3. The first round-shape wave is called the i_1' wave and the second drawn-out one the i_1 wave, because both are considered as being caused by the reduction of manganese^{III} to manganese^{II}. The average currents of both waves are represented with $\bar{i}_1'$ and $\bar{i}_1$, respectively.

The effect of pH on the polarogram of manganese^{III} in a tartrate solution is shown in Fig. 4. Because manganese^{II} was not readily oxidised by air at a pH less than 11, the pH of the solution was adjusted with perchloric acid after manganese^{II} is oxidised to manganese^{III} at pH 11·8. With decreasing pH, the minimum becomes less pronounced, the i_1' wave shifts to less negative potentials and $(\bar{i}_1')_l$ increases to reach the limiting value that is the same as $(\bar{i}_1)_l$, where $(\bar{i}_1')_l$ and $(\bar{i}_1)_l$ represent the limiting currents of the corresponding waves. At pH 9·1 a polarogram with no minimum is obtained (see curve 1), while in 0·1*M* sodium hydroxide the i_1' wave almost vanishes

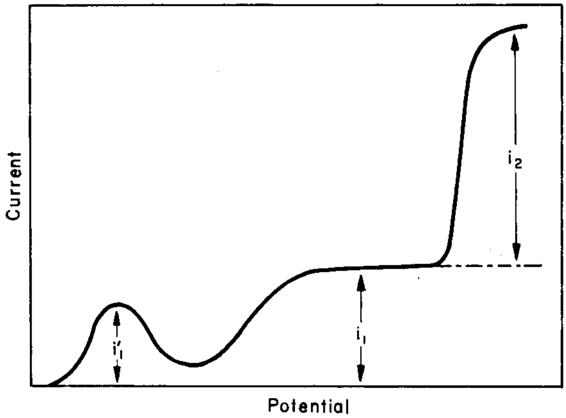

FIG. 3.—Synoptical denotation of the manganese^{III} wave in alkaline tartrate solution.

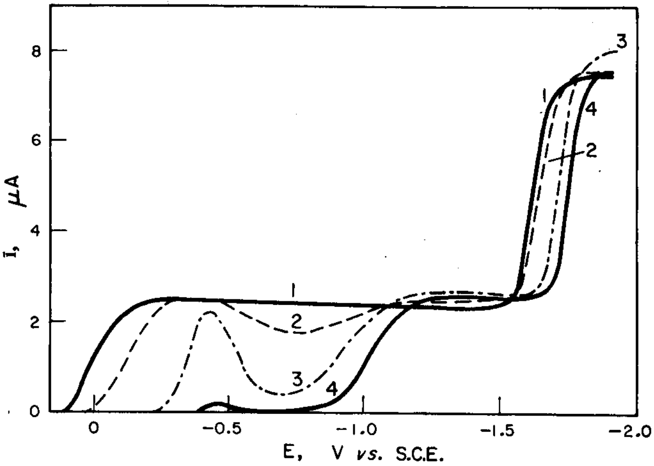

FIG. 4.—Polarograms of 1·0 mM of manganese^{III} at various pH in the solutions containing 0·25*M* sodium tartrate, 0·001 % of gelatin and Britton-Robinson buffer (curves 1, 2 and 3) or 0·1*M* sodium hydroxide (curve 4):

(1) pH 9·1; (2) pH 10·5; (3) pH 11·8.

(curve 4). The decreasing pH also shifts the i_2 wave to less negative potentials. The shifts of the i_1' and the i_2 waves to more negative potentials with increasing pH indicate that hydrogen ions are taken up when the manganese^{III} and the manganese^{II} complexes are reduced to the corresponding lower oxidation states.

The effect of tartrate ion on the reduction wave was investigated by recording the polarograms in the presence of varied concentrations of sodium tartrate. With increasing concentrations of tartrate, the i_1' wave started at more negative potentials and the $\bar{i}_1'$ current decreased; the $\bar{i}_l/10$-potentials, which mean the potentials at $\bar{i} = \bar{i}_l/10$, were found to be $-0{\cdot}24$ V at $0{\cdot}10M$ and $-0{\cdot}35$ V at $0{\cdot}70M$ of tartrate, respectively. This suggests that tartrate ions are liberated when the manganese^{III} complex is reduced to the bivalent state. As for the i_1 wave, the potentials were not appreciably affected with the increase of tartrate concentration, but the limiting current was depressed to a great extent. The value of $(\bar{i}_1)_l/C$ measured at $-1{\cdot}55$ V *vs.* SCE varied from $2{\cdot}7_7$ μA/mM to $2{\cdot}2_5$ μA/mM, when the tartrate concentration was changed from $0{\cdot}25M$ to $0{\cdot}63M$. This decrease may be attributed to the increasing number of tartrate ions co-ordinating.

In Fig. 5 are given the polarograms which were obtained at various concentrations of tartrate but at a constant ionic strength, being adjusted with potassium nitrate. The same decrease in the limiting current of the i_1 wave with increasing tartrate concentrations was observed. These polarograms in Fig. 5 present, however, not only the affect of tartrate but also the affect of potassium nitrate on the reduction wave. A separate experiment indicated that upon the addition of potassium nitrate, the i_1' wave was suppressed and the i_1 wave was shifted to less negative potentials. The former seems to be from the presence of nitrate ions and the latter from potassium ions.

Effect of surface-active substances

By the addition of gelatin both the i_1' and the i_1 wave are depressed (Fig. 6). This agrees with the fact that gelatin adsorbs on the mercury surface in the wide range of potentials. On the other hand, the addition of thiocyanate ions, which adsorb mainly at the positive branch of the electrocapillary curve, depressed only the i_1' wave (Fig. 7). A most interesting effect of a surface-active substance was found when trimethyloctadecylammonium chloride, $(CH_3)_3(C_{18}H_{37})N^+Cl^-$, (denoted as TMOAC) was added to the solution. Fig. 8 presents the polarograms obtained at various concentrations of TMOAC. The addition of a small concentration of TMOAC depresses both the i_1' and the i_1 wave. At higher concentrations of TMOAC, however, the electron transfer at the i_1' wave is further decelerated but that at the i_1 wave is considerably accelerated. The dual (deceleration and acceleration) effect of surface active substance has been reported by Frumkin and coworkers,[9] who found that tetrapentylammonium ion, at its lower concentration, accelerates the reduction of tetrachloroplatinate$^{(II)}$ but, at its higher concentration, decelerates the reduction. The dual effect of TMOAC on the reduction of manganese^{III} in an alkaline tartrate solution is seen also from the current-time curves during the life of a mercury drop measured at $-0{\cdot}82$ V *vs.* SCE (Fig. 9).

Electrode process of manganese^{III} in an alkaline tartrate solution

As mentioned above, the results obtained with the Kalousek polarograms suggest that the manganese^{III} species produced by the air oxidation in an alkaline tartrate

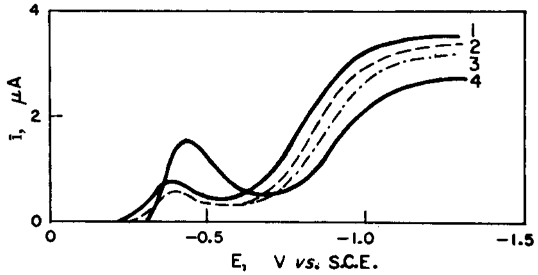

FIG. 5.—Polarograms of 1·2 mM of manganese^{III} in the solutions of pH 11·8 and ionic strength 2·0 (adjusted with potassium nitrate) containing Britton-Robinson Buffer, various concentrations of sodium tartrate and 0·001 % of gelatin. Concentrations of sodium tartrate: (1) 0·125*M*; (2) 0·250*M*; (3) 0·375*M*; (4) 0·625*M*.

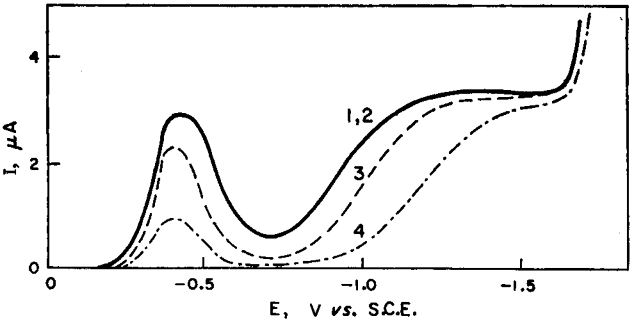

FIG. 6.—Effect of gelatin on the polarograms of 1·2 mM of manganese^{III} in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate. Concentrations of gelatin: (1) 0; (2) 0·001 %; (3) 0·005 %; (4) 0·01 %.

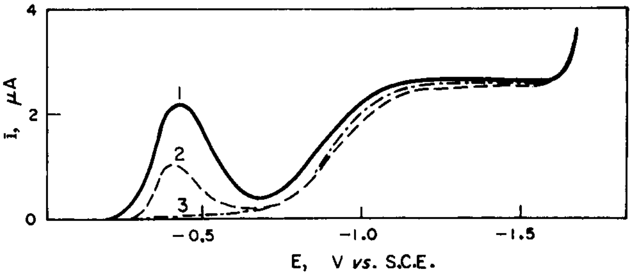

FIG. 7.—Effect of thiocyanate ions on the polarograms of 1·0 mM of manganese^{III} in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and 0·001 % of gelatin. Concentrations of thiocyanate: (1) 0; (2) 0·010*M*; (3) 0·030*M*.

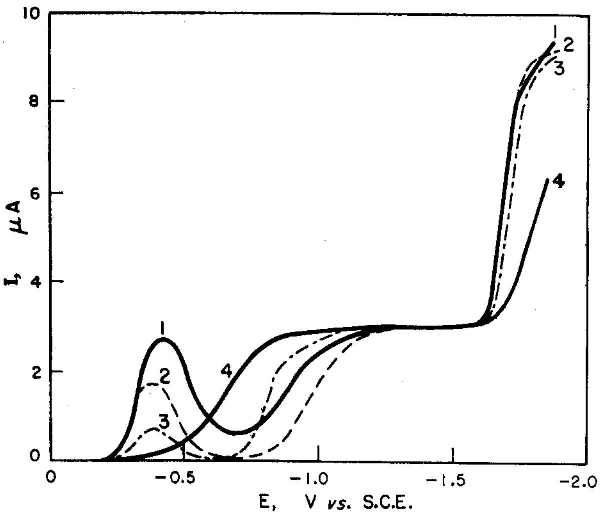

FIG. 8.—Polarograms of 1·2 mM of manganese^{III} in the solution of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate in the absence (curve 1) and in the presence of 0·13 mM (2), 0·25 mM (3) and 1·2 mM (4) of trimethyloctadecylammonium chloride.

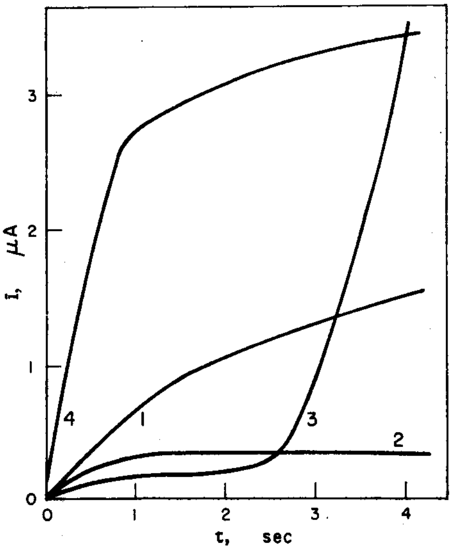

FIG. 9.—Current-time curves at —0·82 V *vs.* SCE obtained with the same solutions as given in Fig. 8.

solution is hydroxotartratomanganate(III) complex, $Mn(OH)_p(tar)_q^{z-}$ (tar = tartrate), which is considered to be negatively charged in an alkaline solution.

The plot of $\log \bar{i}/(\bar{i}_d - \bar{i})$ against E for the i_1' wave gives a straight line with a slope of approximately 80 mV, which is somewhat greater than expected for the reversible one-electron reduction. The i_1 wave, on the other hand, is drawn-out and of an irreversible type. The measurement of a.c. polarograms confirmed the degree of irreversibility of both i_1' and i_1 waves. The value of $i_p/n\bar{i}_d\sqrt{t_d}$[10] of the i_1' wave, where i_p means a peak current of a.c. polarogram, $\bar{i}_d$ the diffusion current of d.c. polarogram, n the number of electrons involved in the electrode process and t_d the drop time, was calculated to be 25·4 $\mho A^{-1}$ sec$^{-1/2}$, which is about half of that for the reduction of zinc^{II} in 1*M* potassium nitrate solution, but approximately 4 times greater than that for the reduction of nickel^{II} in 0·1*M* potassium chloride solution. The i_1 wave, on the other hand, shows no peak on the a.c. polarograms.

The hydroxotartratomanganate(III) complex is reduced to the corresponding manganese^{II} complex. Because the complex is negatively charged, it can readily approach to the positively charged electrode surface and, consequently, the electrode process takes place with lower activation energy. The rate of electron transfer is of the magnitude of the quasi-reversible type, being estimated from the value of $i_p/n\bar{i}_d\sqrt{t_d}$ and the shape of the Kalousek polarogram. This electrode process is, however, easily hindered by the addition of a small amount of surface active substance that is specifically adsorbed in the positive branch of electrocapillary curve, such as thiocyanate ions, because the complex is not specially surface active, as was confirmed by the measurement of the electrocapillary curve.

This electrode process is decelerated by the decrease in positive charge and the increase in negative charge of the electrode. This causes a minimum on the current-potential curve as has been reported in the case of the reduction of many anions.[11] The minimum is not observed at lower pH, because of the decrease in negative charge of the manganese^{III} complex species.

In the negative branch of the electrocapillary curve, the electroreduction of the complex with higher activation energy takes place. This seems partly because of the electrostatic repulsion between the complex and the negatively charged electrode. The addition of cations that adsorb on the electrode surface neutralises the negative charge of the electrode or those cations act as bridging ions so that the activation energy is lessened and the electron transfer is accelerated.

Zusammenfassung—Die Bildung von Mangan(III)-Komplexen durch Luftoxydation von Mangan(II) in alkalischer Tartratlösung wurde durch Messung der Gleichstrom- und der Kalousek-Polarogramme bestätigt. Ein deutliches Minimum erschien im pH-Bereich von 10 bis 13 auf dem Polarogramm. Der Einfluß des pH, der Konzentration von Natriumtartrat und von oberflächenaktiven Stoffen auf das Polarogramm wurden untersucht und die Elektrodenprozesse von Mangan(III) in alkalischer Tartratlösung diskutiert.

Résumé—La formation de complexes du manganèse(III) par oxydation à l'air du manganèse(II) en solution tartrique alcaline a été confirmée par la mesure du courant continu et les polarogrammes de Kalousek. On a observé un minimum net sur le polarogramme, dans l'intervalle de pH 10–13. On a étudié les effets, sur le polarogramme, du pH, de la concentration du tartrate de sodium, et des substances tensio-actives; on discute des processus à l'électrode du manganèse(III) en solution tartrique alcaline.

REFERENCES

[1] I. M. Kolthoff and J. I. Watters, *Ind. Eng. Chem., Analyt.*, 1943, **15**, 8.
[2] J. V. A. Novák, J. Kůta and J. Říha, *Chem. Listy*, 1953, **47**, 649.
[3] E. Svátek, Z. Roubal and R. Přibil, *ibid.*, 1953, **47**, 1472.
[4] E. T. Verdier, *Coll. Czech. Chem. Comm.*, 1939, **11**, 233.
[5] M. Kalousek, *ibid.*, 1948, **13**, 105.
[6] N. Tanaka, R. Tamamushi and M. Kodama, *Bull. Chem. Soc. Japan*, 1960, **33**, 14.
[7] N. Tanaka, R. Tamamushi and A. Takahashi, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3016.
[8] Wang Er-Kong and A. A. Vlček, *ibid.*, 1960, **25**, 2089.
[9] A. N. Frumkin, O. A. Petrii and N. V. Nikolaeva-Fedorovich, *Doklady Akad. Nauk S.S.S.R.*, 1961, **136**, 1158.
[10] M. Senda, M. Senda and I. Tachi, *J. Electrochem. Soc. Japan*, 1959, **27**, 83.
[11] A. N. Frumkin and N. Nikolaeva-Fedorovich, *Progress in Polarography*, edited by Zuman and Kolthoff. Interscience Publishers, N.Y., 1962, Chapter IX.

Talanta, 1964, Vol. 11, pp. 231 to 239. Pergamon Press Ltd. Printed in Northern Ireland

A MODIFICATION OF THE EXPONENTIAL EXCHANGE LAW IN HETEROGENEOUS SYSTEMS

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Summary—The exponential exchange law for heterogeneous systems can be applied to isotope exchange between solid salts and their saturated solutions after allowance is made for the initial rapid exchange between the solution and the crystal surface. For a variety of salts it is possible to get information on the dynamic equilibrium between the surface and the interior of the crystals. Experimental results are presented for the chromates of silver, barium and lead. Silver chromate exchanges rapidly with silver ion, without showing significant exchange with chromate ion. Recrystallisation effects are evident in the chromates of barium and lead.

INTRODUCTION

THE exchange between fresh precipitates and saturated solutions has been the subject of study by Kolthoff and his associates since 1933.[1] The incorporation of radioisotope in the solid was attributed to recrystallisation of the solid, thus exposing continuously new surface. Most of this work preceded the formulation of the "exponential exchange law" by McKay in 1938.[2]

This law, as applied to heterogeneous systems, states that

$$Rt = -\frac{A\,.\,B}{A+B}\ln(1-F) \tag{1}$$

where R = moles of tagged material crossing the interface per time unit,
t = time,
A = moles of solid,
B = moles of tagged solute in solution,
F = fraction of exchange, which can be expressed in count rates of aliquots of the solution.

If the solution contains all the radioactivity initially,

$$F = \frac{S_0 - S_t}{S_0 - S_\infty}$$

in which S_0 = cpm at $t = 0$; S_t = cpm at $t = t$, and S_∞ = cpm at isotopic equilibrium throughout the system.

Experimental results show clearly that the exponential exchange law is not valid in exchange between an initially inactive solid and its saturated radioactive solution.

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* From Ph.D. dissertation, submitted by L. J. Parcell to the Graduate School of Arts, and Sciences, University of Virginia, June, 1963.

An example of the results of such an experiment is shown in Fig. 1, curve I. A rapid initial increase, followed by a slower, but linear increase of $-\log(1-F)$ with time is shown.

Because the initial rapid exchange is caused by exchange with the surface, there is a simple method of separating the fast and slow exchanges mathematically. We studied the slow exchange process by application of a modification of the exponential exchange law. Apparent deviations from this law, as caused by the initial rapid surface exchange, are eliminated by this modification.

DISCUSSION

One essential requirement for conformity with the exponential exchange law of heterogeneous systems is a relatively rapid isotopic equilibrium in each phase compared to the rate-determining step in exchange at the interface. Generally the surface of crystals is considered to be part of the solid phase. However, in isotopic exchange it is necessary to treat the crystal surface and the solution as one single phase, and the interior of the crystals as the second phase. This approach is made because the rate-determining step in the slow exchange process is either between the surface and the interior of the crystals, or in the interior of the crystals, but certainly not between solution and surface.

The initial condition for the slow exchange process is ideally a solution in isotopic equilibrium with the surface, without any activity being present in the interior of the crystals. An approximation to this condition is obtained by extrapolation of the linear part of curve I in Fig. 1 to $t = 0$; the F value obtained by this extrapolation pertains to surface exchange only.

The slow exchange process starts with an initial activity in solution reduced by surface exchange from S_0 to $S_0{}^*$. The value of $S_0{}^*$ is obtained from $S_0{}^* = \frac{B}{M_s + B}$, in which B is the number of moles of tagged species in solution, and M_s is the number of moles of the same chemical species in the surface of the crystals. This modification of S_0 to $S_0{}^*$ is not dependent upon the mechanism of the secondary slow exchange process. The newly defined $S_0{}^*$ can be used to check the validity of the exponential exchange law for the slow secondary exchange. It is determined from the F value obtained by extrapolation of $-\log(1-F)$ to $t = 0$.

The exponential exchange law needs modification when it is applied to the slow exchange process after isotopic equilibrium is established between the solution and the surface. It takes the form

$$Rt = -\frac{(A - M_s)(B + M_s)}{A + B} \ln(1 - F^*) \qquad (2)$$

where A, B, R and t are as in equation (1), M_s = number of moles in the surface, and

$$F^* = \frac{S_0{}^* - S_t}{S_0{}^* - S_\infty}.$$

A plot of $-\log(1 - F^*)$ versus time is given in Fig. 1, curve II. For this example of exchange between solid silver chromate and its saturated solution containing tagged silver nitrate, a linear relationship is obtained. A small positive deviation from the origin on the time abscissa would be expected, because the slow exchange process cannot become significant until some exchange has occurred between the solution and the surface. However, the linear relationship is an indication of a rate-determining step in exchange between the surface and the interior of the crystals.

More indication of the validity of this form of the exchange law is obtained by changing variables which should not affect the chemical composition at the interfaces. The weights of identical crystals taken for an experiment can be varied. R should be directly proportional to the interfacial area, or to the weight of solid used. It is convenient to define K by $R = K \, . \, A$, because K is independent of the weight of solid used, and K is expressed in reciprocal time units. Because M_s is generally small compared with A, the following expression is obtained:

$$\mathrm{d}\frac{[-\ln(1 - F^*)]}{\mathrm{d}t} = K\frac{A + B}{B + M_s}. \tag{3}$$

The two criteria, a linear relationship between log $(1 - F^*)$ and time, and a value of K independent of the amount of solid used, can be applied to a variety of systems. Results of our studies show that the exchange between silver ion in solution and solid silver chromate conforms to equations (2) and (3) in all cases.

Deviations from this exchange law are evident in exchange between either solid lead chromate or barium chromate, and tagged chromate in their saturated solutions, because a linear relationship is not obtained. The deviations do not necessarily show that there is no rate-determining step in exchange somewhere between the surface and the interior of the crystals. The requirements for conforming with equations (2) and (3) include:

(*a*) a relatively rapid equilibrium of isotopes in each of the two parts in which the system is separated;

(*b*) a constant interfacial area during the experiment. Recrystallisation generally decreases this area, and solutions should be used in which recrystallisation is kept to a minimum. Shaking may rupture crystals, causing increase of the surface area.

(*c*) no unidirectional recrystallisation. Some freshly prepared crystals (*e.g.*, lead chromate) may change to a more stable crystal lattice, or they may undergo a chemical change. A temporary heterogeneous isotopic distribution may result from such transitions.

Generally the number of moles of tagged species in solution is much smaller than the number of moles of solid, because the most accurate determinations of M_s are obtained when $B \cong M_s$. The value of S_∞ is much smaller than that of either S_0 or $S_0{}^*$ in our determinations. If S_∞ is ignored in calculation of F and of F^*, the following approximate values are obtained:

$$-\ln(1 - F) \cong -\ln\frac{S_t}{S_0} \quad \text{and} \quad -\ln(1 - F^*) \cong -\ln\frac{S_t}{S_0{}^*}.$$

The variable with time is S_t in both cases, and identical slopes are obtained for the linear part of curve I and curve II in Fig. 1. The modification of the exchange law causes a change in the relationship between the slope and K, without changing the slope significantly.

In any experiment with systems conforming to the modified exchange law, a value of the rate constant K can be found, giving the number of moles of tagged species crossing the interface per time unit per mole of solid present. More information on the actual mechanism can be obtained by determination of K at various temperatures, at different compositions of the saturated solution, and for changes of size and shape of crystals. The effect of some of these variables on the exchange between silver ion and silver chromate is shown under *Experimental.*

EXPERIMENTAL

Reagents

Radioactive silver: 0·546 g of Analysed Reagent grade silver foil was irradiated in the 1-Mw reactor at the University of Virginia to give about 1 mcurie of ^{110m}Ag. The silver was dissolved in dilute nitric acid, and suitable portions of the solution were used for exchange studies. Excess of nitric acid was removed by evaporation under infrared radiation followed by heating at 110° for 1 hr. The residue was dissolved in distilled water.

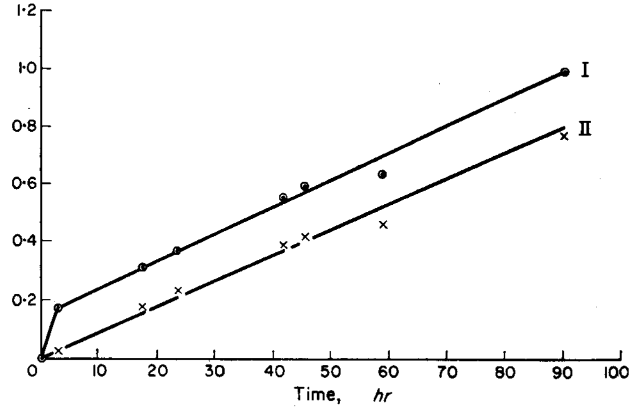


FIG. 1.—A typical exchange between solid silver chromate and tagged silver ion in 50% ethanol.

I: Ordinate is $-\log(1 - F)$
II: Ordinate is $-\log(1 - F^*)$

Radioactive chromium: ^{51}Cr in the form of chromate was obtained from Squibb in 50-μ curie amounts. Also 10 mcuries of $^{51}CrCl_3$ in HCl (Oak Ridge National Laboratories) was used. Chloride, which was present in the solutions from both sources, must be removed, because it would cause precipitates of silver chloride in silver ion-silver chromate exchange. This removal was done by addition of excess of 6N nitric acid and sufficient inactive potassium chromate to make a final solution of about $10^{-6}M$ chromate. Evaporation removes chloride as NOCl, and reduces chromate to chromic ion. Oxidation back to chromate was done by excess of hydrogen peroxide after adjustment of the pH to 10 with potassium hydroxide. After evaporation of this solution to remove hydrogen peroxide, the residue was dissolved in distilled water, and the pH was adjusted to 7·0 with 0·001M perchloric acid.

s-Diphenyl carbazide reagent for chromate contained 0·25 g of Eastman reagent (Cat. 618) and 4 g of phthalic anhydride (Matheson Coleman and Bell, Cat. 2619) in 100 ml of 95% ethanol.

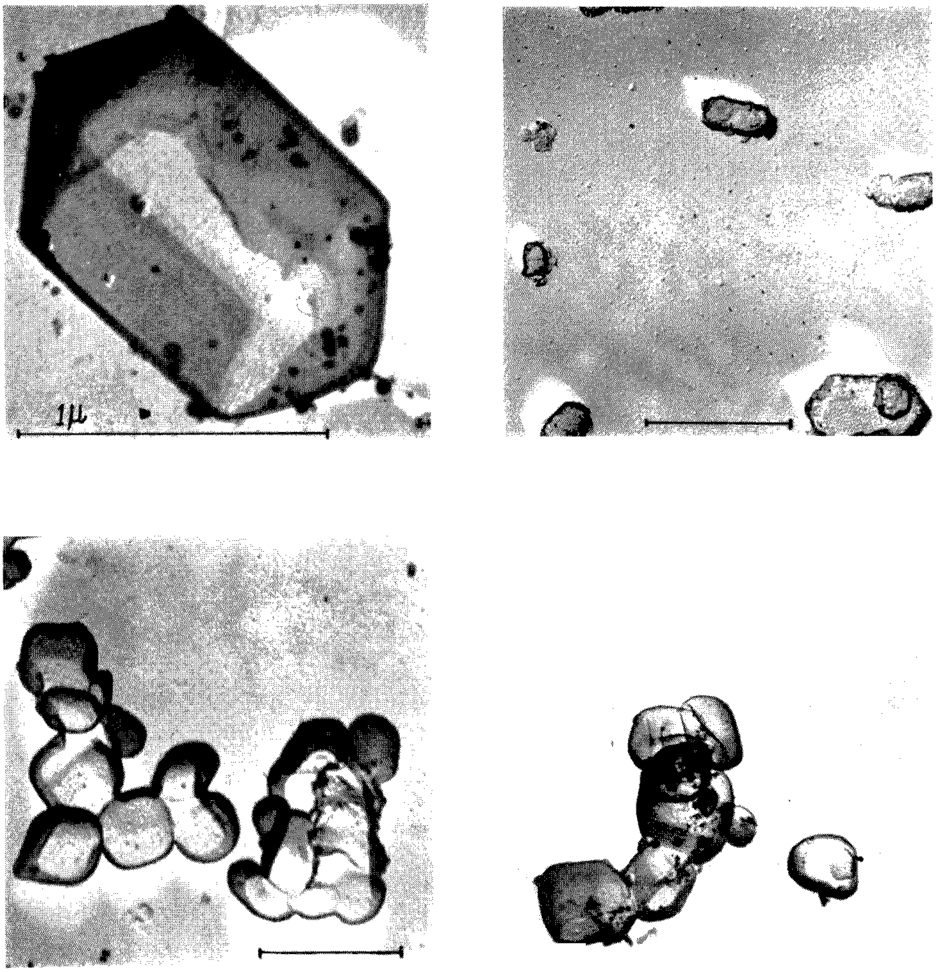
Silver nitrate and potassium nitrate: 0·100M stock solutions were prepared from Baker and Adamson AR-grade chemicals, and distilled water.

Barium chloride: Baker and Adamson purified $BaCl_2 \cdot 2H_2O$ was used to prepare a 0·1M solution in distilled water.

Lead perchlorate: Baker's N.F. PbO was added slowly to 70% Baker and Adamson reagent-grade perchloric acid. The solution was filtered to remove traces of PbO_2, and was diluted to 2M. The pH was adjusted to 2·5 with dilute perchloric acid.

Acetate buffer: 160 g of sodium acetate and 6·0 g of glacial acetic acid, both AR-grade were dissolved in 2 litres of distilled water.

Ethanol: Either Pharmco or USI ethanol was used in the experiments.



B

D

PLATE I.—Photomicrographs A B C D

Preparations of precipitates

In general, stock solutions of reagents were filtered through fine glass filters before use in precipitations. Supersaturated mixtures were prepared by rapid mixing of equivalent solutions in a 400-ml polyethylene beaker. A Sargent Cone-Drive Stirrer, with a glass impeller having two blades of 2-cm length each, was used at 300 rpm for mixing. After about 3 min most of the precipitate had formed, and the suspension was poured into 200-ml wide-mouth bottles, and was centrifuged for 5 min at 2000 rpm. After decantation, the precipitate was washed twice with distilled water, then with inactive solution of the same composition as the exchange solution.

Precipitates of silver chromate were prepared by rapid mixing of 200 ml of solutions of silver nitrate and of potassium chromate to give initial concentrations of silver chromate of $8{\cdot}75 \times 10^{-4}M$, and of $5{\cdot}00 \times 10^{-3}M$. The chromate solution contained 10 ml of acetate buffer.

Solid barium chromate was formed by mixing $0{\cdot}005M$ solutions of barium chloride and of potassium chromate. Lead chromate was formed in mixtures of $0{\cdot}010M$ lead perchlorate and of $0{\cdot}010M$ potassium chromate. The pH of both solutions was adjusted to 1·8 before mixing.

Exchange experiments

The precipitates were left in the 200-ml centrifuge bottles after the last washing. The appropriate tagged solution was added (generally 100 ml), and the resulting suspension was kept agitated using a Burrell wrist-action shaker. The bottles were kept in a water bath at $25 \pm 0{\cdot}1°$. At intervals the liquid and the solid phase were separated by centrifugation. Aliquots of 0·500 ml were taken from the solution for activity measurements. At the end of the experiment the crystals were filtered into fine sintered-glass crucibles, and their weight was determined after drying at 110°. The chromate concentration in solutions containing silver nitrate was determined by the diphenylcarbazide method. The absorbance at 540 mμ was compared with the absorbance of standard solutions of chromate. The presence of silver ion did not affect the absorbance.

The counting of the aliquots was done in a scintillation well counter (Baird Atomic, Model 810) connected to a single channel analyser, which counted in the photopeak of the isotope. The counting of ^{51}Cr samples was done at approximately the same time for each experiment in order to avoid decay corrections.

Because the surface area was poorly reproduced in duplicate experiments, the values of K determined from the count rates were divided by the percentage of surface found by exchange. K is expected to be proportional to the specific surface if the crystals are of identical shape, but of different size. $K/\%$ surface gives a measure of the exchange per unit area of the surface.

RESULTS

Electron micrographs were made of carbon replicas of silver chromate crystals formed from stirred supersaturated solutions at various initial concentrations. Typical results are presented for precipitates from $8{\cdot}75 \times 10^{-4}M$ Ag_2CrO_4 (micrograph A, Plate I), and from $5{\cdot}00 \times 10^{-3}$ M Ag_2CrO_4 (micrograph B, Plate I). The pyramid faces formed on crystals at the lower concentration are not visible on crystals from the higher concentration. Agglomeration is evident in the second micrograph.

Aging for three days in $10^{-4}M$ $AgNO_3$ in 50% ethanol gives an indication of surface changes on the large crystals, without causing change in the appearance of the agglomerates of small crystals. Micrograph C, Plate I, shows the effect of aging on crystals from $8{\cdot}75 \times 10^{-4}M$ Ag_2CrO_4, and micrograph D, Plate I, indicates little change of the agglomerates formed from $5{\cdot}00 \times 10^{-3}M$ Ag_2CrO_4.

Table I shows results obtained using precipitates formed under identical conditions. Nevertheless, surface exchange varied from 2·79% to 2·02%, and K from $2{\cdot}14 \times 10^{-3}$ to $1{\cdot}52 \times 10^{-3}$/hr. However, $K/\%$ surface remains fairly constant, indicating little, if any, effect of the three-fold increase of the silver ion concentration in solution on the rate of exchange.

Table II shows the effect of increase of supersaturation in precipitate formation on exchange. The exchange surface and the exchange rate constant are smaller than

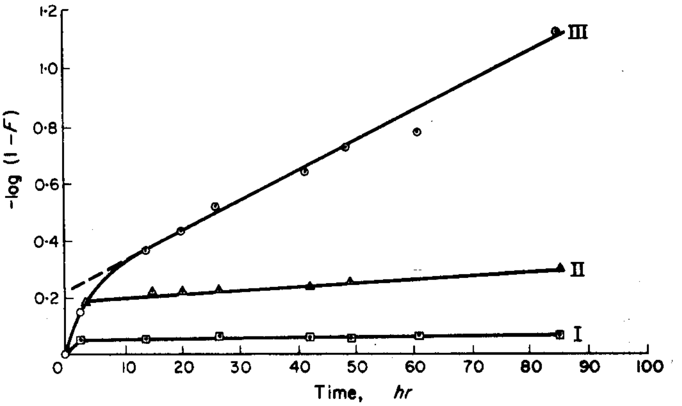


FIG. 2.—Comparison of silver and chromate exchange.
I—1·00 × $10^{-4}M$ $K_2{}^{51}CrO_4$
II—8·77 × $10^{-6}M$ ${}^{51}CrO_4{}^{=}$ in 1·0 × $10^{-4}M$ $AgNO_3$
III—1·00 × $10^{-4}M$ ${}^{110m}Ag$ NO_3
(Ag_2CrO_4 from solution 8·75 × $10^{-4}M$ in Ag_2CrO_4 initially.)

TABLE I.—EXCHANGE BETWEEN CRYSTALS FROM 8·75 × $10^{-4}M$ Ag_2CrO_4 AND TAGGED Ag^+ IN 50% ETHANOL.

100 ml of 1·0 × $10^{-4}M$ $AgNO_3$ A = 1·34 × 10^{-4} moles			100 ml of 3·0 × $10^{-4}M$ $AgNO_3$ A = 2·13 × 10^{-4} moles		
Time, *hr*	S_t	$-\log(1-F)$	Time, *hr*	S_t	$-\log(1-F)$
0	13,470	—	0	13,360	—
2·7	9,230	·179	4·2	11,160	0·088
17·3	7,190	·309	17·1	10,000	0·145
23·4	6,160	·380	40·9	8,240	0·247
41·6	4,640	·530	65·4	6,550	0·374
45·5	4,030	·605	71·8	6,190	0·418
50·8	3,720	·654	95·0	5,260	0·508
59·3	2,920	·801	120·7	4,680	0·583
90·4	2,210	·992			

% surface = 2·79.
K = 2·14 × 10^{-3}/hr.
K/% surface = 7·7 × 10^{-4}/hr.

% surface = 2·02.
K = 1·52 × 10^{-3}/hr.
K/% surface = 7·5 × 10^{-4}/hr.

TABLE II.—EXCHANGE BETWEEN CRYSTALS FROM 5·0 × $10^{-3}M$ Ag_2CrO_4 AND TAGGED Ag^+ IN 50% ETHANOL.

100 ml of 3 × $10^{-4}M$ $AgNO_3$ A = 35·9 × 10^{-4} moles			100 ml of 6 × $10^{-4}M$ $AgNO_3$ A = 35·3 × 10^{-4} moles		
Time, *hr*	S_t	$-\log(1-F)$	Time, *hr*	S_t	$-\log(1-F)$
0	10,890	—	0	12,130	—
3·0	4,250	·416	5·0	6,310	·289
21·7	3,530	·495	21·0	5,080	·378
28·0	3,320	·526	52·1	4,400	·451
45·6	2,690	·621	65·5	3,920	·503
50·5	2,680	·623			
66·4	2,400	·672			

% surface = 1.25.
K = 2,14 × 10^{-4}/hr.
K/% surface = 1·7 × 10^{-4}/hr.

% surface = 1.47.
K = 2·53 × 10^{-4}/hr.
K/% surface = 1·7 × 10^{-4}/hr.

TABLE III.—COMPARISON OF SILVER AND CHROMATE EXCHANGE

100 ml of $10^{-4}M$ $AgNO_3$ in 50% ethanol tagged with $^{51}CrO_4^{2-}$ $A = 0{\cdot}60 \times 10^{-4}$ moles of Ag_2CrO_4 from $8{\cdot}75 \times 10^{-4}M$ Ag_2CrO_4			100 ml of $1 \times 10^{-4}M$ $AgNO_3$ in 50% alcohol tagged with ^{110m}Ag $A = 0{\cdot}73 \times 10^{-4}$ moles of Ag_2CrO_4 from $8{\cdot}75 \times 10^{-4}M$ Ag_2CrO_4		
Time, *hr*	S_t	$-\log(1 - F)$	Time, *hr*	S_t	$-\log(1 - F)$
0	15,920		0	6,570	—
2·7	10,440	·190	2·7	4,685	·156
14·2	9,600	·222	14·2	3,090	·362
20·0	9,560	·225	20·1	2,695	·433
26·2	9,460	·230	26·2	2,320	·511
41·8	9,310	·238	41·8	1,865	·632
49·1	8,880	·257	49·2	1,590	·721
61·3	7,900	·309	61·3	1,480	·762
85·5	8,130	·298	85·5	905	1·108
	% surface = ·85. $K = 4{\cdot}7 \times 10^{-5}$.			% surface = 3.4. $K = 2{\cdot}7 \times 10^{-3}$.	

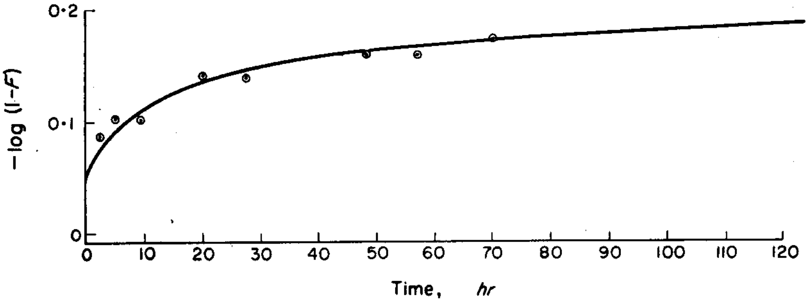


FIG. 3.—Exchange between solid $PbCrO_4$ and $1{\cdot}00 \times 10^{-4}M$ $K_2{}^{51}CrO_4$ in 50% ethanol. $A = 7{\cdot}44 \times 10^{-4}$ moles.

those found under the conditions in Table I. A two-fold increase of the silver ion concentration does not change the value of K/% surface.

Table III shows the results of exchange between portions of the same batch of precipitate of silver chromate and either $^{51}CrO_4^{=}$, or ^{110m}Ag ion in 50% ethanol. Surface exchange is only 0·85 mole%, and $K = 4{\cdot}7 \times 10^{-5}$/hr for chromate exchange in a saturated solution of silver chromate in $10^{-4}M$ silver nitrate. The exchange with silver ion gives 3·4 mole% of surface, and $K = 3{\cdot}3 \times 10^{-3}$/hr. Fig. 2 shows the difference in exchange rate, and it includes exchange in $1{\cdot}00 \times 10^{-4}M$ $K_2{}^{51}CrO_4$ (curve I). The unfavourable ratio of B/A prevents determination of K from the slope of curve I.

Our results indicate a ratio of eight readily exchangeable silver ions to one exchangeable chromate at the surface. Preliminary experiments with other precipitates gave a similar ratio.

Chromate exchange between solid lead chromate or barium chromate, and solutions tagged with chromate is illustrated in Figs. 3 and 4. The slopes of the curves change continuously, and therefore the modified exchange law cannot be applied to this exchange.

CONCLUSIONS

The modified exponential exchange law can be applied to exchange between solid silver chromate and solutions containing either tagged silver ion, or tagged chromate. The difference in the rate constant, K, between the exchange with silver ion and that with chromate is appreciable. Recrystallisation alone cannot account for the exchange mechanism. Moreover, recrystallisation would change the area of the interface, causing deviation from the exchange law. This process of recrystallisation may account mainly for the results obtained in exchange between $^{51}CrO_4^{2-}$ and solid lead or barium chromate.

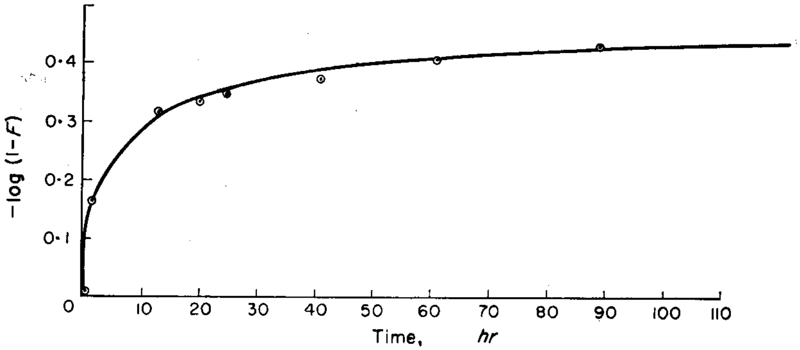


FIG. 4.—Exchange between solid $BaCrO_4$ and $1{\cdot}00 \times 10^{-4}M\ K_2{}^{51}CrO_4$ in 50% ethanol. $A = 12{\cdot}2 \times 10^{-4}$ moles.

The difference between the exchange surface found in chromate and silver ion exchange with silver chromate cannot be explained before more extensive studies are completed. Possible causes include adsorbed silver salt during the preparation of the precipitate, and more surface layers with readily exchangeable silver than layers containing similar chromate ions.

Calculating $K/\%$ surface, in evaluation of the properties of precipitates, gives interesting results. According to the results in Tables I and II, the exchange rate per unit area is much smaller for the agglomerates of small particles than for the relatively large crystals. Rapid aging during the precipitation, causing agglomeration, could decrease the areas of faces on which exchange mainly takes place, possibly the pyramidal faces shown in electron micrograph A.

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Zusammenfassung—Das exponentielle Austauschgesetz für heterogene systeme kann auf den Isotopenaustausch zwischen festen Salzen und ihren gesättigten Lösungen angewandt werden, wenn man den anfänglichen schnellen Austausch zwischen Lösung und Kristalloberfläche berücksichtigt. Bei verschiedenen Salzen ist es möglich, Aufschluß über das dynamische Gleichgewicht zwischen Oberfläche und Innerem der Kristalle zu erhalten. Experimentelle Ergebnisse an den Chromaten von Silber, Barium und Blei werden angegeben. Silberchromat tauscht mit Silberionen rasch aus, mit Chromat nicht merklich. Bei Barium- und Bleichromat sind deutlich Rekristallisationseffekte zu beobachten.

Résumé—On peut appliquer la loi exponentielle d'échange des systèmes hétérogènes aux échanges isotopiques entre les sels solides et leurs solutions saturées, après avoir apporté une correction pour l'échange initial rapide entre la solution et la surface du cristal. Pour des sels divers, il est possible d'obtenir des renseignements sur l'équilibre dynamique entre la surface et l'intérieur des cristaux. On présente des données expérimentales pour les chromates d'argent, de baryum et de plomb. Le chromate d'argent montre un échange rapide avec l'ion argent, sans échange important avec l'ion chromate. Les effets de la recristallisation sont évidents pour les chromates de baryum et de plomb.

REFERENCES

[1] I. M. Kolthoff and C. Rosenblum, *J. Amer. Chem. Soc.*, 1933, **55**, 2656.
[2] H. McKay, *Nature*, 1938, **142**, 997.

Talanta, 1964, Vol. 11, pp. 241 to 245. Pergamon Press Ltd. Printed in Northern Ireland

REACTION OF IRON^{III} WITH HYDROXYAMINOACIDS

N,N-DIHYDROXYETHYLGLYCINEIRON^{III}

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Summary—The stoichiometry and equilibrium for the reaction of iron^{III} with *N,N*-dihydroxyethylglycine in aqueous medium has been investigated. Iron^{III} is shown to form only a 1:1 complex with the ligand; previous reports of a 2:3 complex are demonstrated to be erroneous, and probably resulted from non-equilibrium titration measurements. Using a modified Bjerrum titration procedure, the equilibrium constant for the formation of the 1:1 complex at 25° has been determined to be $3{\cdot}8 \times 10^{-8}$ moles^2/litre^2. Attempts to differentiate between alternative structures for the complex are inconsequential, because the complex exists only in aqueous medium, where the ligand hydroxyl groups exchange rapidly with solvent water.

PREVIOUS studies in our laboratories[1,2] have investigated the use of *N,N*-dihydroxyethylglycine (DHEG) as a complexing agent to control the mechanism for hydrolysis of iron^{III} and permit the precipitation from aqueous solution of crystalline iron^{III} oxide as β-FeOOH. Because the role of the tetradentate DHEG ligand appears to be unique in facilitating the precipitation of the crystalline oxide, the stoichiometry and equilibrium for the reaction of DHEG with iron^{III} have been investigated in order to provide further information concerning the reactions involved.

In an aqueous solution of pH 2–4, iron^{III} reacts with DHEG to form the complex (I)

$$\mathrm{Fe^{+3} + HG + 2H_2O \rightarrow \underset{(I)}{Fe(OH)_2G} + 3H^+}. \tag{1}$$

In this reaction DHEG is assumed to behave as a monoprotic acid HG, which coordinates in four positions about the iron^{III} ion. Formula (I) is identical with that proposed by Toren and Kolthoff[3] from polarographic studies of the reaction of iron^{II} and iron^{III} with DHEG. It conflicts with the earlier work by Martell and co-workers[4,5] who assumed DHEG to react as a triprotic acid H_3A, according to equation (2):

$$\mathrm{Fe^{+3} + H_3A + 2H_2O \rightarrow \underset{(II)}{Fe(H_2O)_2A} + 3H^+}, \tag{2}$$

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where water fills the two co-ordination positions allotted to the hydroxyl ions in equation (1). Formulae (I) and (II) differ in that Martell *et al.* assumed the two hydroxyl groups in the co-ordinated ligand to be more acidic than water, whereas the conventional interpretation assumes the co-ordinated water to be the more acidic. Because the iron^{III} complex is stable only in aqueous solution, where the ligand hydroxyl groups should exchange rapidly with the solvent, differentiation between the two structures would be trivial if Martell *et al.* had not reported the formation, above pH 8, of a second binuclear complex, $Fe_2A_3^{-3}$, which was not observed in the other studies.[2,3]

The present work is a reinvestigation of the stoichiometry for the reaction between iron^{III} and DHEG, and the equilibrium constant for equation (1) has been determined. The previous evidence[4] for the formation of the $Fe_2A_3^{-3}$ complex is demonstrated to be erroneous, and probably resulted from non-equilibrium titration measurements.

EXPERIMENTAL

DHEG was purified by recrystallising twice from ethanol. Standard iron^{III} solutions were prepared by dissolving iron wire in hydrochloric acid and diluting to volume.

Oxidation of aliquots of the iron solution was effected by treating with hydrogen peroxide and decomposing the excess hydrogen peroxide by boiling. The stability constant of the iron^{III}-DHEG complex was determined by titration at 25° (*vide infra*). Before titration, the acidity of the iron^{III} solution was reduced to pH 2·0 ± 0·05 by neutralisation with gaseous ammonia to prevent the excess acid from consuming an appreciable portion of the added base. The DHEG complexing agent was then added, and the solution was diluted to volume and titrated with standard sodium hydroxide solution. Details have been described elsewhere.[3]

NMR spectra were recorded using a Varian A-60 spectrometer.

RESULTS

Acidic solutions containing 0·001M iron^{III} and 0·0011M to 0·02M DHEG were titrated with standard base. The titration curves exhibit two end-point inflections. The first of these occurs when the ratio m, the number of moles of base added per mole of iron^{III} in solution, equals three. This end-point corresponds to the titration of the three equivalents of hydrogen ion liberated according to equation (1) or (2). Using a modified Bjerrum-type procedure, the equilibrium constant, K, for equation (1) may be calculated from the titration results, where

$$K = \frac{[\mathrm{Fe(OH)_2G}][\mathrm{H^+}]^3}{[\mathrm{Fe^{III}}][\mathrm{HG}]}. \tag{3}$$

If n is the number of moles of complex formed per mole of total iron^{III}, for $n = 0·5$,

$$[\mathrm{Fe^{III}}] = [\mathrm{Fe(OH)_2G}],$$

and

$$K = [\mathrm{H}]^{+3}/[\mathrm{HG}]. \tag{4}$$

In acid solution the concentrations of $[\mathrm{OH^-}]$ and $(\mathrm{G^-}]$ are negligibly small, and HG may be readily calculated as

$$[\mathrm{HG}] = \frac{\{(3 - a)C_G - [\mathrm{H^+}]\}K_1}{4[\mathrm{H^+}] + 3K_1}, \tag{5}$$

where a is the number of moles of base added per mole of total DHEG, K_1 is the first acid dissociation constant[3,4] of the protonated amino acid, H_2G^+, and C_G is the total concentration of DHEG in solution. Knowing [HG] as a function of the pH during the titration, n is given by

$$n = \frac{C_G - [HG]\{[H^+]/K_1 + 1\}}{C_{Fe}} \qquad (6)$$

where C_{Fe} is the concentration of total iron^{III} in solution. Plotting [H$^+$] and [HG] as a function of n, values corresponding to $n = 0{\cdot}5$ permit the calculation of K in equation (4). Using this procedure, the pH of the solutions in the vicinity of n $\simeq$ 0·5 remains sufficiently acidic (pH $<$ 3·6) to prevent interference from the incipient precipitation of $Fe(OH)_3$.

TABLE I—DETERMINATION OF EQUILIBRIUM CONSTANT FOR $Fe(OH)_2G$.
(Ionic strength = 0·01. T = 25°. $C_{Fe} = 1{\cdot}00\ 10^{-3}M$.)

C_G/C_{Fe}	$(pH)_{n=0{\cdot}5}$	$10^3\ [HG]_{n=0{\cdot}5}$	$10^8\ K$
1·1	3·55	0·490	4·58
1·1	3·60	0·492	3·21
2·0	3·54	1·26	1·90
2·0	3·55	1·17	1·91
5·0	3·34	3·61	2·64
5·0	3·36	3·74	2·23
10·0	3·10	8·43	5·82
10·0	3·10	6·21	8·21
			avg. = (3·8 ± 1·8)
			pK = 7·4

Table I indicates typical values for K calculated from titration results for various ratios of C_G/C_{Fe}. Our value of pK = 7·4 is in reasonable agreement with the equally precise value of 6·1 calculated from the polarographic data of Toren and Kolthoff.[3] Their K_{III} is related to our K by

$$K \equiv K_{III}K_w^2K_2,$$

in which K_w is the autoprotolysis constant for water and K_2 is the second ionisation constant for DHEG.[3,4]

The position of the second end-point inflection in the titration curves depends upon the concentration of excess DHEG in solution. For C_G/C_{Fe} ratios of 2, 5, 10 and 20, the end-point occurs when m equals 5, 8, 13 and 23, respectively. If three moles of base are required to titrate the acid liberated by the formation of the iron^{III}-DHEG complex according to equation (1) or (2), the remainder $(m - 3)$ represents the amount of base required to precipitate $Fe(OH)_3$ from the complex and to neutralise the excess DHEG in solution. These latter reactions may be represented by the general equation:

$$Fe(OH)_2G + (m - 4)HG + (m - 3)OH^- \rightarrow Fe(OH)_3 + (m - 3)G^- + (m - 4)H_2O. \qquad (6)$$

As written, this reaction requires all of the iron^{III} in solution to be precipitated upon addition of $(m - 3)$ moles of base.

The amount of $Fe(OH)_3$ precipitated during the titrations was analysed gravimetrically by ignition to Fe_2O_3 and also by dissolving the hydrous oxide in acid and titrating with standard cerium^{IV} solution. Because the aggregation and precipitation of the colloidal iron^{III} hydroxide is very slow under these conditions, if solutions to which *m* moles of base had been added were allowed to settle for 1–3 days, quantitative precipitation of the iron was achieved in every case. The ability to precipitate the iron under such conditions has been the basis for the procedure for the quantitative precipitation of crystalline iron^{III} oxide as β-FeOOH.[1]

DISCUSSION

The present studies have confirmed the stoichiometry of reaction (1) [or (2)] in which iron^{III} forms only a 1:1 complex with DHEG in acid medium. They contrast sharply with those of Martell *et al.* (*loc. cit.*), who reported an unspecified partial precipitation of iron which led them to suggest a second binuclear complex $Fe_2A_3^{-3}$*. We conclude that the latter complex is not formed, for it is not thermodynamically stable, and iron^{III} is quantitatively precipitated under the experimental conditions.

The propriety of formula (I) or (II) in solution cannot be determined. Intuitively, structure (I) is preferred, because the ligand hydroxyl groups should have approximately the same acidity as in ethanol, and should be considerably less acidic than water (K_3 and K_4 for DHEG are too small to be measured in aqueous medium). However, the relative acidities of $HOCH_2CH_2$— and H_2O when co-ordinated by iron^{III} have not been determined. On the basis of polarisability and ligand-field strength, it is predicted that H_2O will dissociate to a considerably greater degree than will CH_3CH_2OH when co-ordinated by iron^{III}; and hydrolysed species such as $Fe(OH)^{+2}$ and $Fe(OH)_2^+$ are well known. NMR spectra of solutions of DHEG in 99·5% D_2O show, in addition to the HOD singlet, two triplets and one singlet, each of relative area 2, which are characteristic of the three methylene groups in the ligand molecule. The absence of a more detailed spectrum, including a triplet of relative area 1 at the proper chemical shift for the ethanolic —OH group, indicates that the ligand hydroxyl groups do exchange rapidly with the solvent water. Because the exchange is rapid, differentiation between structures (I) and (II) is inconsequential.

Zusammenfassung—Stöchiometrie und Gleichgewicht der Reaktion von Eisen(III) mit N,N-dihydroxyäthylglycin in wässrigem Medium wurden untersucht. Es wird gezeigt, dass Eisen(III) nur einen 1:1-Komplex bildet; frühere Angaben über einen 2:3-Komplex sind falsch und basierten wahrscheinlich auf Messungen ausserhalb des Gleichgewichts. Mit einer modifizierten Titrationsmethode nach Bjerrum wurde eine Gleichgewichtskonstante von $3{,}8\cdot10^{-8}$ mol^2/l^2 für die Bildung des 1:1-Komplexes bei 25°C erhalten. Strukturangaben für den Komplex sind nocht sinnvoll, da er nur in wassrigem Medium existiert, wo die als Liganden auftretenden Hydroxylgruppen rasch mit dem Lösungsmittel ausgetauscht werden.

Résumé—La stoechiométrie et l'équilibre de la réaction du fer(III) avec l'acide N,N′ dihydroxyéthyl amino-acétique en milieu aqueux ont été étudiés. Il est établi que le fer(III) forme seulement un complexe 1:1 avec le complexant; il est démontré que le complexe 2:3 décrit précédemment n'existe pas et résultait probablement de mesures faites avant que l'équilibre soit réalisé. En utilisant une méthode de Bjerrum modifiée, la constante d'équilibre de formation du complexe 1:1 déterminée à 25°C est $3{,}80 \,.\, 10^{-8}$ moles^2/l^2. Les structures du

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* Martell *et al.*[4] do not report if approximately one-third of the total iron was precipitated as required by the stoichiometry of the reaction.

complexe sont sans intérêt puisqu'il existe seulement en milieu aqueux où les liaisons entre les groupes hydroxyles s'échangent rapidement avec l'eau du solvant.

REFERENCES

[1] E. R. Nightingale, Jr. and R. F. Benck, *Analyt. Chem.*, 1960, **32**, 566.

[2] R. F. Benck, M. S. thesis, University of Nebraska, 1958.

[3] P. E. Toren and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1955, **27**, 2061.

[4] S. Chaberek, Jr., R. C. Courtney and A. E. Martell, *ibid.*, 1953, **75**, 2185.

[5] R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr. and A. E. Martell, *ibid.*, 1958, **80**, 2121.

Talanta, 1964, Vol. 11, pp. 247 to 254. Pergamon Press Ltd. Printed in Northern Ireland

POTENTIOMETRIC STUDY OF THE COMPLEXES OF MERCURY^{I} WITH PYROPHOSPHATE, TRIPHOSPHATE AND TETRAPHOSPHATE

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Summary—The dimer of mercury^{I} forms stable complexes with polyphosphates. The stabilities of these complexes decrease slightly as the chain length increases. Because of the strong tendency of mercury^{I} to associate with hydroxide ions, the mixed complex species containing both polyphosphate and hydroxide ions were found to be the predominant species in slightly alkaline solutions. In polyphosphate solutions, polarographic waves of Hg^{I} and Hg^{II} are obtained at similar potentials, because the Hg^{II} reacts chemically with the mercury of the drop to form Hg^{I} complexes before the electrode reaction occurs. Similar anodic waves are obtained in the presence or absence of mercury ions in solution because of the formation of mercury^{I} complexes. The tetraphosphate complexes which have not been studied before, and their over-all complexity constants in the presence of $1M$ KNO_3 and $0{\cdot}15M$ guanidinium ion at 25°, are:

$Hg_2(P_4O_{13})^{4-}$, $10^{7\cdot32}$; $Hg_2(P_4O_{13})_2{}^{10-}$, $10^{9\cdot88}$;
$Hg_2(P_4O_{13})(OH)^{5-}$, $10^{15\cdot26}$; $Hg_2(P_4O_{13})(OH)_2{}^{6-}$, $10^{22\cdot45}$.

INTRODUCTION

THE nature and stability of the various species formed by mercury are of considerable importance because of the unique application of mercury in polarography. The reversibility of a large number of mercury electrode reactions, and the possibility of forming either mercury^{I} or mercury^{II} species, enhance the importance of these studies.

Relatively few stable complexes of mercury^{I} have been prepared. In the presence of strong complexing agents, such as ethylenediamine[1] and ethylenediaminotetraacetate,[2] the mercury^{I} disproportionates to form the stable soluble mercury^{II} complex and free mercury as a black colloid. However, Yamane and Davidson[3] have shown that mercury^{I} forms stable complexes with pyrophosphate, triphosphate, oxalate, dimethylmalonate and succinate, and have determined their stability constants by means of potentiometric measurements using the mercury pool electrode. In the present study, a similar behaviour was established in tetraphosphate solutions, and the existence of mercury^{I} complexes in pyro- and triphosphate solutions was confirmed. By maintaining constant conditions, it was possible to establish trends in stability with increasing phosphate chain length.

Preliminary experiments were performed with the dropping mercury electrode, and electrode reversibility was established by the continuity of these waves across the

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zero-current axis. However, because of the requirement of very dilute mercury solutions to avoid precipitation in acidic solutions, the quiet mercury pool was used in the final potential measurements.

Previous studies of tetraphosphate and its acidic properties are described in an earlier paper.[4] Details of the theoretical approach to the interpretation of the potential values in the presence of several complexing species by Leden's method have also been described.[5-7] The existence of the mixed hydroxide complexes and values for their complexity constants were obtained both by determinants and graphically by slope intercept plots.

Consider the equilibrium between a metal ion and several ligands involving only molecular complexes:

$$\mathrm{M + iA + jB + kC \rightleftarrows MA_iB_jC_k}$$

for which one can write the over-all complexity constant

$$\beta_{\mathrm{ijk}} = \mathrm{[MA_iB_iC_k]/[M][A]}^j\mathrm{[B]}^j\mathrm{[C]}^k.$$

The corresponding equation and equilibrium constant for the stepwise addition of any one ligand, for example, C, are

$$\mathrm{MA_iB_jC_k + C \rightleftarrows MA_iB_jC_{k+1}}$$

$$K^{\mathrm{ijk}}_{\mathrm{ijk+1}} = \mathrm{[MA_iB_jC_{k+1}]/[MA_iB_jC_k][C]}.$$

In this series of studies, A indicates H^+; B, the polyphosphate ion; and C, the hydroxide ion while i, j and k are small integers or zero. Ionic charges are omitted in general expressions. Brackets indicate concentrations, and parentheses indicate activities. For example, the over-all complexity constant for $Hg_2(P_4O_{13})(OH)^{5-}$ is indicated as follows

$$\beta_{011} = \mathrm{[Hg_2(P_4O_{13})(OH)^{5-}]/[Hg_2{}^{2+}][P_4O_{13}{}^{6-}](OH)^-}.$$

The stepwise constant for the addition of another OH^- ion to this species is

$$\mathrm{K}^{011}_{012} = \mathrm{[Hg_2(P_4O_{13})(OH)_2{}^{6-}]/[Hg_2(P_4O_{13})(OH)^{5-}](OH)^-}.$$

As previously discussed, the simultaneous association of H^+ with the complexed polyphosphate and OH^- with the metal ion, if this should occur, cannot be detected, because this is equivalent to the addition of a molecule of water. Only the addition of one in excess causes a potential shift.

Mixed complexes containing hydroxide ions were found to be present throughout most of the pH range in which the mercury$^{\mathrm{I}}$ complexes were stable. As a result, the association of hydrogen ions with the complexed polyphosphate, which played an important role in the copper-polyphosphate systems, was generally not observed.

Leden's first function, F_0, has the general form

$$\mathrm{F_0} = \mathrm{antilog}\,\frac{E_{\mathrm{aq}} - E_{\mathrm{c}}}{S} = \sum_{\mathrm{i=O}}^{\mathrm{i=N}}\ \sum_{\mathrm{j=O}}^{\mathrm{j=N'}}\ \sum_{\mathrm{k=O}}^{\mathrm{k=N''}} \beta_{\mathrm{ijk}}\mathrm{[A]^i[B]^j[C]^k}.$$

In this equation, E_{aq} is the spontaneous reversible electrode or half-wave potential of a particular concentration of aquo metal ion in a solution containing no complexing agent, while E_{c} is the corresponding potential of the same total concentration of a metal ion in the presence of a fixed excess concentration of ligands and at the same temperature. In order to maintain a constant ionic strength, both solutions should contain the same concentration of supporting electrolyte in large excess. The symbol

S indicates $2{\cdot}303\ RT/nF$ of the Nernst equation, and has the value 0·02958 for Hg_2^{2+} at 25°.

EXPERIMENTAL

The experimental procedure and methods for preparing the polyphosphates have already been described.[4,8,9] However, the experiments were all performed in the presence of $1M$ alkali metal ions. In the tetraphosphate experiments, guanidinium ions were also present, because the ligand was purified by crystallisation in the form of the guanidinium salts. Because alkali metal ions are known to form complexes with polyphosphates,[8,9] we have adopted the expedient followed by Yamane and Davidson of calculating the free ligand concentration on the basis of the experimentally determined apparent acidity constants after correcting for the concentration of ligand bound in the mercury complex. This is equivalent to ignoring the association of alkali metal ions with the free or complexed ligand, and is justified if the activity of the alkali metal ions and, consequently, the apparent acidity constants, are kept essentially constant. This phenomena is discussed in some detail at the end of the paper on copper triphosphate complexes.[6] The last two acidity constants are indicated by the symbols K_N and K_{N-1}. For tetraphosphate, they have the form

$$K_6 = (H^+)[P_4O_{13}{}^{6-}]/[HP_4O_{13}{}^{5-}],$$

$$K_5 = (H^+)[HP_4O_{13}{}^{5-}]/[H_2P_4O_{13}{}^{4-}].$$

Following the procedure of Pugh,[10] a stock solution of mercury$^{\mathrm{I}}$ nitrate was prepared by shaking red mercury$^{\mathrm{II}}$ oxide, mercury and nitric acid until, after the addition of sodium chloride to precipitate mercury$^{\mathrm{I}}$, a filtered aliquot gave no test for mercury$^{\mathrm{II}}$ ion with H_2S. The stock solution was then standardised by titrating with a standard sodium chloride solution using 0·04% bromophenol blue as the indicator. In this paper, the concentration of mercury$^{\mathrm{I}}$ will be indicated in terms of the molar concentration of Hg_2^{2+} which is one-half that of the mercury$^{\mathrm{I}}$ atoms.

Mercury$^{\mathrm{II}}$ nitrate was prepared by dissolving metallic mercury with freshly boiled concentrated nitric acid and diluting. The mercury$^{\mathrm{II}}$ nitrate solution was standardised against standard thiocyanate using ferric alum as the indicator, according to the method of Kolthoff and Sandell.[11]

The most extensive preliminary polarographic experiments were performed in the presence and absence of pyrophosphates. Just as was observed by Kolthoff and Miller,[12] the spontaneous potentials of similar concentrations of aquo mercury$^{\mathrm{I}}$ and aquo mercury$^{\mathrm{II}}$, namely 1·22 mM, were identical, but the diffusion coefficient of the latter was somewhat smaller. In the presence of $5 \times 10^{-2}M$ $Na_4P_2O_7$, $1M$ $NaNO_3$ and 0·0005% methyl red, the waves coincided even in the diffusion-current region. Both waves were continuous across the zero-current axis, which proved that the electrode reaction was reversible. The absence of any black colloidal mercury in the mercury$^{\mathrm{I}}$ solution indicated that a stable mercury$^{\mathrm{I}}$ complex was present. Furthermore, a mercurous chloride precipitate was obtained upon the addition of excess chloride ion. A similar test of the mercury$^{\mathrm{II}}$ pyrophosphate solutions was negative. After removing oxygen of the air by flushing with nitrogen, both solutions were shaken in the presence of an excess of free mercury. The quantitative conversion of the mercury$^{\mathrm{II}}$ pyrophosphate complex to mercury$^{\mathrm{I}}$ complex, upon contact with free mercury, was shown by the previously described titration with standard NaCl.

These experiments confirm the observation of Yamane and Davidson that both mercury$^{\mathrm{I}}$ and mercury$^{\mathrm{II}}$ form stable complexes. However, just as Kolthoff and Miller[12] observed for the aquo system, the mercury$^{\mathrm{II}}$ complex is chemically reduced to the mercury$^{\mathrm{I}}$ complex upon diffusing to the drop surface, so that, in both cases, it is the mercury$^{\mathrm{I}}$ complex which determines the electrode potential. The diffusion currents for similar concentrations of the Hg^{2+} and Hg_2^{2+} coincide, so that their diffusion coefficients are similar. This probably results from the relatively large contribution of the complexed polyphosphate to the size of ions.

The remainder of the study was made with mercury$^{\mathrm{I}}$ solutions. When the solution was made more acidic, the waves decreased in height and a precipitate was observed. By reducing the concentration of mercury to the order of $10^{-5}M$, this complication was eliminated. The accuracy of measuring the spontaneous potential of the dropping electrode was greatly decreased because of the relatively large magnitude of the residual current, so that it was found expedient to replace the dropping mercury electrode with a quiet mercury pool. Typical potential values for the mercury$^{\mathrm{I}}$ pyro-, tri- and tetraphosphate systems are given in Tables I, II and III, respectively. The absence of mercury$^{\mathrm{II}}$ in these solutions was established by the previously discussed qualitative tests.

The acidic limit was indicated by the failure of the electrode to undergo further change in potential. The alkaline limit, which was manifested by unsteady potentials, was ascribed by Yamane and Davidson to the formation of solid HgO. The pH was varied without altering the total mercury$^{\mathrm{I}}$ and ligand concentrations, by mixing various portions of a solution which was acid-free with a similar solution which contained nitric acid. The experiments were performed as rapidly as possible after acidifying the solution, to minimise hydrolysis of the polyphosphates to lower phosphates. Fresh solutions were prepared after a few measurements. The extent of hydrolysis was readily shown by the phosphomolybdate test for orthophosphates.

TABLE I.—POTENTIAL VALUES FOR PYROPHOSPHATE-MERCURY^{I} SYSTEM

Part A: $[Hg_2^{2+}]_t = 1{\cdot}22 \times 10^{-5}M$;
$[P_2O_7^{4-}]_t = 0{\cdot}05M$;
$[Na^+]_t = 1{\cdot}0M$;
$E_{aq} = 0{\cdot}3852$ v *vs.* S.C.E.

Part B: like A, but $1M$ Na^+ replaced by $1M$ K^+, $E_{aq} = 0{\cdot}3753$ v.

pH	$E_{aq} - E_c$	$-\log [P_2O_7^{4-}]$	log F_1	log F_2	log F_{2a}	log F_{3a}
Part A						
9·62	0·3086	1·30	11·71	13·01	16·07	20·40
9·53	0·3035	1·30	11·55	12·85	15·99	20·40
9·16	0·2860	1·31	10·97	12·28	15·67	20·38
9·04	0·2822	1·31	10·84	12·15	15·60	20·40
8·58	0·2722	1·33	10·53	11·85	15·31	20·34
8·02	0·2640	1·41	10·33	11·72		
7·50	0·2539	1·59	10·17	11·74		
6·96	0·2332	1·94	9·82	11·71		
6·53	0·2125	2·32	9·48	11·67		
5·93	0·1819	2·97	9·12	11·67		
5·29	0·1482	3·85	8·86			
5·03	0·1349	4·27	8·83			
4·56	0·1098	5·12	8·83			
Av. limiting constant			8·83	11·72	15·07	20·40
Part B						
10·00	0·3223	1·41	12·20	13·71	16·28	20·08
9·59	0·3043	1·42	11·70	13·12	16·04	20·00
8·95	0·2863	1·45	11·12	12·56	15·85	
8·60	0·2802	1·49	10·96	12·44	15·87	
8·00	0·2652	1·66	10·72	12·26		
7·63	0·2539	1·86	10·49	12·27		
7·04	0·2276	2·33	10·02	12·27		
6·64	0·2075	2·72	9·73	12·27		
6·25	0·1891	3·16	9·55			
5·91	0·1721	3·59	9·40			
5·43	0·1481	4·30	9·30			
4·99	0·1288	5·06	9·41			
4·63	0·1132	5·74	9·56			
Av. limiting constant			9·25	12·27	15·85	20·05

RESULTS AND DISCUSSION

Using the symbol Pp to indicate the polyphosphate ion and omitting the complex ion charge for simplicity, the predominant species necessary to account for the potential shift as a function of pH and polyphosphate concentration were Hg_2Pp, Hg_2Pp_2, HgPpOH and $HgPp(OH)_2$. The corresponding Leden function F_0 is:

$$F_0 = \text{antilog}\,(E_{aq} - E_c)/S = 1 + \beta_{010}[Pp] + \beta_{020}[Pp]^2 + \beta_{011}[Pp](OH^-) + \beta_{012}[Pp](OH^-)^2$$

Subtracting unity, and dividing through by [Pp], yields the Leden function, F_1, thus:

$$F_1 = (F_0 - 1)/[Pp] = \beta_{010} + \beta_{020}[Pp] + \beta_{011}(OH^-) + \beta_{012}(OH^-)^2.$$

The limiting constant value of F_1 at low values of [Pp] and (OH^-) or the F_1 intercept of a graph of F_1 versus [Pp] at low or constant values of (OH^-) is equal to β_{010}. In the

TABLE II.—POTENTIAL VALUES FOR TRIPHOSPHATE-MERCURY^{I} SYSTEM

Part A: $[Hg_2^{2+}]_t = 1\cdot22 \times 10^{-5}M$;
$[P_3O_{10}^{5-}]_t = 0\cdot05M$;
$[Na^+]_t = 1\cdot0M$;
$E_{aq} = 0\cdot3852$ v *vs.* S.C.E.

Part B: like A but $1M$ Na^+ replaced by $1M$ K^+, $E_{aq} = 0\cdot3753$ v.

pH	$E_{aq} - E_c$	$-\log [P_3O_{10}^{5-}]$	log F_1	log F_2	log F_{2a}	log F_{3a}
Part A						
9·34	0·2791	1·31	10·74	12·05	15·40	20·05
9·03	0·2617	1·31	15·15	11·46	15·12	20·07
8·53	0·2330	1·32	9·19	10·51	14·65	20·07
8·07	0·2092	1·34	8·41	9·72	14·24	20·05
7·60	0·1927	1·40	7·91	9·22	13·95	20·04
7·32	0·1859	1·47	7·75	9·09	13·85	
6·73	0·1696	1·76	7·49	8·97	13·68	
6·38	0·1578	2·02	7·35	8·90		
6·03	0·1460	2·34	7·27	8·90		
5·73	0·1359	2·64	7·23	8·82		
5·53	0·1292	2·86	7·23			
5·28	0·1207	3·16	7·24			
Av. limiting constant			7·64	8·90	13·65	20·05
Part B						
9·99	0·3157	1·46	12·13	13·59	16·25	20·37
9·40	0·2877	1·46	11·18	12·64	15·78	20·37
9·01	0·2639	1·47	10·39	11·86	15·38	20·34
8·66	0·2440	1·48	9·72	11·28	15·08	20·31
8·35	0·2261	1·50	9·14	10·62	14·74	
8·09	0·2156	1·53	8·81	10·29	14·60	
7·69	0·2019	1·62	8·44	9·93	14·44	
7·28	0·1895	1·79	8·19	9·72	14·30	
7·04	0·1821	1·94	8·09	9·67	14·26	
6·60	0·1682	2·28	7·96	9·62	14·21	
Av. limiting constant			8·02	9·65	14·22	20·35

sodium pyrophosphate study, as shown in Table IA and summarised in the last line of Table IA, the limiting constant value of F_1 in the pH range 4·56–5·29 was $10^{8\cdot83}$, corresponding to the complexity constant for the association of one pyrophosphate with Hg_2^{2+}. Thus:

$$Hg_2^{2+} + P_2O_7^{4-} \rightleftharpoons Hg_2(P_2O_7)^{2-},$$
$$\beta_{010} = [Hg_2(P_2O_7)^{2-}]/[Hg_2^{2+}][P_2O_7^{4-}] = 10^{8\cdot83}$$

In the presence of $1M$ potassium ions, a constant value was not obtained until the additional species $Hg(HP_2O_7^-)$ was assumed to be present. Solving simultaneous equations, assuming these two species to be present, yielded

$$\beta_{1\overset{*}{1}0} = [Hg_2HP_2O_7^-]/[Hg^{2+}][HP_2O_7^{3-}] = 10^{5\cdot94}.$$

Because of the uncertainty of the values available for the more acidic solutions, these constants for species containing associated hydrogen ion cannot be regarded as reliable, so will not be reported,

The next Leden function obtained by subtracting β_{010} from F_1 and dividing by $[P_2O^4{}_7^-]$ was used to calculate β_{020}, thus:

$$F_2 = (F_1 - \beta_{010})/[P_2O_7^{4-}] = \beta_{020} + \beta_{011}(OH^-)/[P_2O_7^{4-}] + \beta_{012}(OH^-)^2/[P_2O_7^{4-}].$$

TABLE III.—POTENTIAL VALUES FOR TETRAPHOSPHATE-MERCURY^{I} SYSTEM

Part A: $[Hg_2^{2+}]_t = 1{\cdot}22 \times 10^{-5}M$;
$[P_4O_{13}^{6-}]_t = 0{\cdot}02491M$;
$[Na^+]_t = 1{\cdot}0M$;
$E_{aq} = 0{\cdot}3852$ v *vs.* S.C.E.

Part B: like A but $1M$ Na^+ replaced by $1M$ K^+, $E_{aq} = 0{\cdot}3753$ v.

pH	$E_{aq} - E_c$	$-\log [P_4O_{13}^{6-}]$	$\log F_1$	$\log F_2$	$\log F_{2a}$	$\log F_{3a}$
Part A						
8·31	0·2863	1·62	11·29	12·91	16·98	22·63
8·14	0·2768	1·62	10·97	12·59	16·83	22·63
8·03	0·2706	1·63	10·77	12·40	16·74	22·64
7·63	0·2483	1·68	10·07	11·75	16·44	22·65
7·33	0·2315	1·74	9·56	11·30	16·22	22·60
7·22	0·2254	1·78	9·40	11·18	16·17	22·61
7·03	0·2170	1·85	9·18	11·03	16·14	22·72
6·71	0·1991	2·03	8·76	10·78	16·02	22·67
6·50	0·1874	2·18	8·51	10·68	15·97	22·65
6·37	0·1801	2·29	8·37	10·64	15·96	22·58
6·34	0·1779	2·31	8·32	10·61	15·93	
6·22	0·1723	2·42	8·24	10·64	15·97	
5·98	0·1578	2·66	7·99	10·61	15·94	
Part B						
8·61	0·2980	1·61	11·68	13·29	17·07	22·45
8·45	0·2885	1·61	11·36	12·97	16·91	22·45
8·35	0·2824	1·62	11·16	12·78	16·81	22·45
8·00	0·2612	1·63	10·45	12·08	16·45	22·42
7·64	0·2409	1·68	9·82	11·50	16·17	22·47
7·35	0·2245	1·74	9·32	11·06	15·94	22·48
7·00	0·2051	1·87	8·80	10·66	15·71	22·51
6·85	0·1983	1·94	8·64	10·56	15·67	22·60
6·68	0·1877	2·05	8·39	10·40	15·52	22·48
6·52	0·1790	2·16	8·21	10·31	15·43	22·41
6·30	0·1678	2·34	8·01	10·23	15·37	22·41
6·15	0·1600	2·48	7·89	10·23	15·35	22·46

From Table I, it is evident that, in the sodium pyrophosphate solution, F_2 has the constant value of $10^{11{\cdot}72}$ from a pH of 8·32 to 5·73.
Thus

$$\beta_{020} = [Hg_2(P_2O_7)_2^{6-}]/[Hg_2^{2+}][P_2O_7^{4-}]^2 = 10^{11{\cdot}72}.$$

Conclusive graphic evidence for the mixed hydroxide species was obtained by a graphic solution of the following Leden function:

$$F_{2a} = (F_2 - \beta_{020})[P_2O_7^{4-}]/(OH^-) = \beta_{011} + \beta_{012}(OH^-).$$

The limiting constant value of F_{2a} or the F_{2a} intercept of a graph in which F_{2a} is plotted versus (OH^-) is equal to β_{011} while the slope is equal to β_{012}. The following Leden functions constant value can be used to confirm β_{012}:

$$F_{3a} = (F_{2a} - \beta_{011})/(OH^-) = \beta_{012}$$

In all of the systems, pyro-, tri- and tetraphosphate, a region was found in which the plot of F_{2a} versus (OH^-) was linear and its intercept value agreed well with the constant value obtained for F_{3a}. The F_{2a} graph was linear above a hydroxide concentration of $5 \times 10^{-6}M$ in pyrophosphate solutions. It was linear above a hydroxide concentration of $4 \times 10^{-5}M$ in the triphosphate solutions and it was linear above a hydroxide concentration of $2 \times 10^{-7}M$ in tetraphosphate solutions. These results constitute conclusive evidence for the existence of the mixed complexes of the type $Hg_2(Pp)(OH)$ and $Hg_2Pp(OH)_2$. For the pyrophosphate system in $1M$ $NaNO_3$:

$$\beta_{011} = [Hg_2(P_2O_7)(OH)^{3-}]/[Hg_2{}^{2+}][P_2O_7{}^{4-}](OH^-) = 10^{15\cdot07}$$

$$\beta_{012} = [Hg_2(P_2O_7)(OH)_2{}^{4-}]/[Hg_2{}^{2+}][P_2O_7{}^{4-}](OH^-)^2 = 10^{20\cdot40}$$

TABLE IV.—SUMMARY OF COMPLEXITY CONSTANTS FOR MERCURY^{I} POLYPHOSPHATE SYSTEM

Medium	pK_N	pK_{N-1}	β_{010}	β_{020}	β_{011}	β_{012}	K^{000}_{010}	K^{010}_{020}	K^{010}_{011}	K^{011}_{011}	K^{020}_{011}
					A-Pyrophosphate						
$1M$ K^+	7·89	5·66	9·25	12·27	15·85	20·05	9·25	3·02	5·20	4·20	3·58
$1M$ Na^+	7·48	5·40	8·83	11·72	15·07	20·40	8·83	2·89	5·33	4·34	3·35
$0·75M$ Na^+	8·00*	5·68*		12·38*	15·64*						3·26*
					B-Triphosphate						
$1M$ K^+	7·36	4·96	7·84	9·47	14·22	20·35	7·84	1·63	6·38	6·13	4·75
$1M$ Na^+	7·00	4·85	7·16	8·90	13·65	20·05	7·16	1·74	6·49	6·40	4·75
$0·75M$ Na^+	7·58*	5·29*		11·23*	15·00*						3·77*
					C-Tetraphosphate						
$1M$ K^+	6·92	5·22	7·32	9·88	15·26	22·45	7·32	2·56	7·94	7·19	5·38
$1M$ Na^+	6·52	4·97	6·98	9·42	15·91	22·64	6·98	2·44	8·93	6·73	6·49

* Results by Yamane and Davidson

A summary of the values obtained for all of the constants, both in the form of over-all constants and stepwise constants, is given in Table IV. These are the mean of all of the values obtained both by determinants considering all species and by slope intercept methods. The corresponding values obtained by Yamane and Davidson are also included. Our results confirm their important discovery of mercury^{I} polyphosphate complexes. The present study indicates the existence of additional species such as Hg(Pp) and the mixed hydroxide complex $HgPp(OH)_2$. Bringing this difference and the difference in experimental conditions into consideration, the quantitative agreement of the two studies is satisfactory. The difference in the values of our constants results in part from the difference in our experimentally determined acidity constants, pK_N and pK_{N-1}, shown in Table IV. Their experimental conditions of 27·4° and $0·75M$ Na^+ are fairly similar to the 25° and $1·0M$ Na^+ used in one phase of our study. In addition, the present study includes the $Hg_2{}^{2+}$ tetraphosphate system.

Several interesting generalisations can be made. Just as was the case in the copper polyphosphate systems but not in the alkali polyphosphate systems, the stepwise constant for the addition of the first polyphosphate, as manifested by the value of K^{000}_{010}, decreases with increasing polyphosphate chain length, but the difference decreases from tri- to tetraphosphate. Of particular significance is the strong tendency of the polyphosphate complex to associate with additional hydroxide ions, as manifested by the magnitudes of K^{010}_{011} and K^{011}_{012}. As might be expected from the above observation, these constants increase in magnitude with increasing polyphosphate chain length. This observation is consistent with the observation by Bennett,[13] as well as Sillén and his coworkers,[14,15] who obtained values of the order of 10^9–10^{10} for the association of one hydroxide with the aquo Hg_2^{2+} ion. These can be compared to our values of $10^{7.94}$ and $10^{8.93}$ for the addition of one hydroxide to $Hg_2P_4O_{13}^{4-}$ in the presence of $1M$ KNO_3 and $1M$ $NaNO_3$, respectively.

Zusammenfassung—Das Dimere von Quecksilber(I) bildet stabile Komplexe mit Polyphosphaten. Die Stabilität dieser Komplexe nimmt mit steigender Kettenlänge schwach ab. Wegen der starken Tendenz von Quecksilber(I) zur Assoziation mit Hydroxylionen wurden in schwach alkalischen Lösungen vorwiegend gemischte Komplexe mit Polyphosphat-und Hydroxylionen gefunden. In Polyphosphatlösungen findet man die polarographischen Wellen von Hg(I) und Hg(II) beim gleichen Potential, da Hg(II) mit dem Quecksilber des Tropfens vor der Elektrodenreaktion chemisch zu Hg(I)-Komplexen reagiert. Ähnliche anodische Wellen findet man mit oder ohne Quecksilberionen in der Lösung wegen der Bildung von Quecksilber(I)-Komplexen. Es wurden folgende bisher nicht untersuchte Tetraphosphatkomplexe mit ihren Gesamt-Komplexbildungskonstanten in Gegenwart von 1m KNO_3 und 0,15m Guanidiniumion bei 25°C gefunden: $Hg_2(P_4O_{13})^{4-}$: $10^{7,32}$; $Hg_2(P_4O_{13})_2^{10-}$: $10^{9,88}$; $Hg_2(P_4O_{13})(OH)^{5-}$: $10^{15,26}$; $Hg_2(P_4O_{13})(OH)_2^{6-}$: $10^{22,45}$

Résumé—Le dimère du mercure(I) forme des complexes stables avec les polyphosphates. La stabilité de ces complexes décroît légèrement lorsque croît la longueur de la chaîne. Par suite de la forte tendance du mercure(I) à s'associer aux ions hydroxyle, on a trouvé que les types de complexes mixtes, contenant à la fois les ions polyphosphate et hydroxyle, sont ceux qui prédominent dans les solutions légèrement alcalines. En solutions polyphosphoriques, les vagues polarographiques de Hg(I) et Hg(II) s'obtiennent à des potentiels similaires, parce que Hg(II) réagit chimiquement avec le mercure de la goutte en formant des complexes de Hg(I) avant que ne se produise la réaction à l'électrode. On obtient des vagues anodiques semblables en présence ou en l'absence d'ions mercure dans la solution, par suite de la formation de complexes de mercure(I). Pour les complexes tétraphosphoriques qui n'ont pas été étudiés auparavant, les constantes globales de complexité en présence de KNO_3 1 M et d'ion guanidinium 0,15 M à 25° sont: $Hg_2(P_4O_{13})^{4-}$, $10^{7,32}$; $Hg_2(P_4O_{13})_2^{10-}$, $10^{9,88}$; $Hg_2(P_4O_{13})(OH)^{5-}$, $10^{15,26}$; $Hg_2(P_4O_{13})(OH)_2^{6-}$, $10^{22;45}$.

REFERENCES

[1] J. I. Watters and J. G. Mason, *J. Amer. Chem. Soc.*, 1956, **78**, 285.
[2] J. I. Watters, J. G. Mason and O. E. Schupp III, *ibid.*, 1956, **78**, 5782.
[3] T. Yamane and N. Davidson, *ibid.*, 1960, **82**, 2123.
[4] J. I. Watters, P. E. Sturrock and R. A. Simonaitis, *Inorg. Chem.*, 1963, **2**, 765.
[5] O. E. Schupp, T. Youness and J. I. Watters, *J. Amer. Chem. Soc.*, 1962, **84**, 505.
[6] P. E. Sturrock, E. D. Loughran and J. I. Watters, *Inorg. Chem.*, 1962, **1**, 457.
[7] O. E. Schupp III, P. E. Sturrock and J. I. Watters, *ibid.*, 1963, **2**, 106.
[8] J. I. Watters, S. M. Lambert and E. D. Loughran, *J. Amer. Chem. Soc.*, 1957, **79**, 3651.
[9] S. M. Lambert and J. I. Watters, *ibid.*, 1957, **79**, 4262.
[10] W. Pugh, *J. Chem. Soc.*, 1957, 1824.
[11] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, 3rd Ed., 1952.
[12] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, 1941, **63**, 2732.
[13] W. H. Bennett, *J. Phys. Chem.*, 1934, **38**, 573.
[14] W. Forsling, S. Heitinen and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.
[15] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, *Stability Constants, Part II, Inorgonic Ligends*. Special Publication No. 7, The Chemical Society, Burlington House W.1., London, 1958.

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ANALYTICAL APPLICATIONS OF RADIOACTIVE VITAMIN B_{12}

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Summary—Radioactive vitamin B_{12} has been employed as an analytical tool, a biochemical tracer and as a diagnostic agent. Of the several labelled modifications reported, only those labelled with cobalt isotopes are useful at physiological dose levels. Because of the high specific activities of (1–200) $\mu c/\mu g$, detection sensitivities in the picagram region are realised with cobalt-labelled vitamin B_{12}. Clinical applications including diagnostic tests for pernicious anaemia in humans, are in a sense analytical procedures, involving as they do measurements of vitamin B_{12} transport. Of more direct analytical character is the application of the isotope dilution method to pharmaceutical preparations, feed concentrates, sewage and fermentation products and crystalline cobalamins. The stability of hydroxocobalamin in pH 4·2 stabilised aqueous solution has been demonstrated by this method. The reverse isotope dilution method also has been very helpful in facilitating stability and degradation studies. The quantitative recovery of unchanged cyanocobalamin from cereals and from capsules containing biological concentrates has been demonstrated by this method. By contrast, the conversion of cyanocobalamin to hydroxocobalamin has been found to occur in the liver of dogs receiving labelled vitamin. An extensive study of protective agents to stabilise vitamin B_{12} in solutions containing ascorbic acid has been performed by this reverse dilution procedure. The sensitivity of the isotope dilution method has been greatly extended to physiological levels by the application of "saturation analysis," an extension of the binding power measurement applied to intrinsic factor concentrates and to animal tissues including serum or plasma.

RADIOACTIVE vitamin B_{12}, in its several forms, has found wide use[1,2] as an analytical tool, as a diagnostic agent and as a biochemical tracer. Even the biological uses have been essentially analytical in nature, because they have involved quantitative determinations of the extent of vitamin adsorption by serum proteins or tissue, absorption or excretion by animals, including man, or stability and degree of conversion to related degradation products.

Vitamin B_{12} is one of a family[3,4] of related, highly coloured, corrinoid compounds called cobalamins or, by a more recent convention, cobamides. The cobalamins are corrin complexes of tervalent cobalt, *i.e.*, porphyrin-like with one bridge carbon atom missing. The best known of the cobalamins is the cyanide complex, cyanocobalamin, the structure of which is shown in Fig. 1, and which is customarily referred to as vitamin B_{12}. It is a neutral, undissociated, relatively stable molecule which can be converted to non-cyano cobalamins photochemically or by catalytic reduction. The major non-cyano analogue, hydroxocobalamin, is a weak base which is converted in the presence of acids into a positive aquocobalamin ion and the respective anion. All non-cyano forms are converted to cyanocobalamin by the addition of cyanide.

LABELLING

Vitamin B_{12} is produced microbiologically by a number of micro organisms incubated in appropriate nutrient media containing sufficient inorganic cobalt for maximal growth. This requires[5] about 2 ppm of cobalt. To produce radioactive cyanocobalamin, the fermentation is usually carried out in the presence of suitable radioactive precursors and, after a rather complicated isolation procedure, the pure crystalline radioactive vitamin is isolated. Radioisotopes which have been successfully incorporated in the cobalamin molecule in this manner are phosphorus-32, carbon-14 and the four long-lived cobalt isotopes. Carbon-14 is also readily introduced[6] as $C^{14}N$ to yield usable specific activities. This modification is, unfortunately, limited by the ease of exchange[7] of the cyanide group, which is in striking contrast to the exchange stability of the central cobalt atom.[8] Cyanocobalamin containing radioactive hydrogen has been prepared by prolonged contact with several curies of tritium gas. Cyanocobalamin containing radioactive cobalt is produced by fermentation in a nutrient medium containing a low concentration of $\lessdot$ 0·1 ppm of radioactive cobalt[9] to maintain a high specific activity of final product. Only radioactive cobalt yields labelled vitamin adequate for studies at physiological levels.

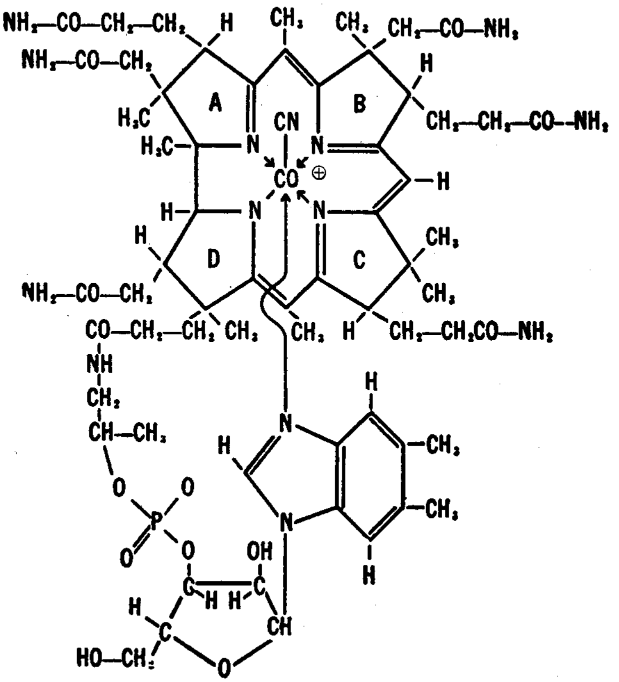

FIG. 1.—Structural formula of vitamin B_{12}.

Cobalt radioisotopes are by far the most useful nuclides with which to label cyanocobalamin. Their radiation properties are tabulated in Table I which lists the type (*i.e.*, beta ray, positron, gamma ray or K-capture X-ray), energy in MeV and frequency of emission of each radiation. Here, 100% signifies that a given ray or particle is emitted with each radioactive disintegration. Relative detection sensitivities will depend on the type of detection devices employed. Detectors, such as

TABLE I—EMISSION BY RADIOACTIVE COBALT ISOTOPES[a]

Cobalt isotope	Half-life	β^- or β^+		γ or K − X	
		MeV	%	*MeV*	%
^{60}Co	5·27y	0·31	100	1·17	100
				1·33	100
^{58}Co	71d	0·47	14·5	0·81	99·5
				0·0064	85·5
				0·51	29·0
^{57}Co	270d	—	—	0·0064	100
				0·123	93
				0·014	93
				0·137	7
^{56}Co	77d	1·50	18·1	0·845	100
				0·0064	81·9
				1·24	70·5
				0·51	36·2
				1·75	17·8
				2·60	15·9
				1·03	15·7
				3·25	12·3
				2·02	11·0

[a] Minor components omitted.

Geiger-Müller and proportional counters, ionisation chambers and liquid scintillation devices, which measure particulate radiation efficiently are excellent for cobalt-56, -58 and -60 but least effective for cobalt-57. This order is reversed when gamma radiation is measured in solid scintillation counters. Thus, cobalt-57 is measured with greatest efficiency in a sodium iodide crystal and cobalt-58 least efficiently. In general, gamma scintillation counting is the most convenient means of determining these radioisotopes.

The characteristics of cyanocobalamin labelled with cobalt isotopes are tabulated in Table II, which shows first the cobalt content of the carrier-free (*i.e.*, 100% isotope) modifications of the vitamin, including the normal, non-radioactive form cobalt-59. This is followed by the maximum specific activities of such carrier-free forms of radioisotopic cobalt (mc/μg) and of the carrier-free labelled cyanocobalamin (in μc/μg) derived therefrom. The next two columns list the specific activities reported or readily available, and the ratios of radioactive cobalt atoms to total cobalt atoms in these preparations. Actually, cyanocobalamin-^{58}Co with specific activities up to 200 μc/μg may be obtained.[10] The last column lists estimated detection sensitivities (in picagrams) computed for a well-type scintillation counter, assuming a detection limit of ±3 cpm. Quantities of the order of picagrams of vitamin can be detected with the radioactive modifications listed, an order of magnitude not readily achieved by other analytical methods.

Vitamin B_{12}-^{57}Co would seem to be the isotopic modification of choice for biological and chemical purposes because of its many desirable properties which may be enumerated as follows:

1. Conveniently long half-life, with attendant flexibility in scheduling the biosynthesis of the radioactive vitamin, and greater shelf-life of the finished product.

2. Less intense gamma radiation, hence greater safety in handling, manufacture and storage of the vitamin.

3. Absence of particulate radiation, with resultant lower radiation exposure of tissue and greater safety for use of the labelled vitamin in humans and animals.

4. Lower self-irradiation exposures, therefore, greater stability of the radioactive vitamin.

5. High detection sensitivity in sodium iodide gamma scintillation phosphors.

TABLE II. CHARACTERISTICS OF CYANOCOBALAMIN CONTAINING RADIOACTIVE COBALT ISOTOPES

	Cobalt in B_{12}, %	Specific activity carrier-free		Available specific activity B_{12}, $\mu c/\mu g$	$\frac{\text{Radioactive Co}}{\text{Total Co}}$	Detection sensitivity, *pg*
		Co, *mc/μg*	B_{12}, $\mu c/\mu g$			
^{60}Co	4·42	1·14	50	$\simeq$1·1	$\frac{1}{47}$	3·6
^{59}Co[a]	4·35	—	—	—	—	—
^{58}Co	4·27	32	1360	$\simeq$5	$\frac{1}{270}$	0·9
^{57}Co	4·20	8·5	357	10–30	$\frac{1}{12\text{–}35}$	0·07–0·2
^{56}Co	4·13	30	1250	$\simeq$5	$\frac{1}{240}$	0·45

[a] Stable cobalt.

For *in vitro* work, as is involved in conventional analytical procedures, cyanocobalamin-^{60}Co is perfectly satisfactory, even preferable, provided subdivision and concentration are such as to assure radiation stability. It has been shown that cyanocobalamin-^{60}Co with a specific activity of $\simeq$1 $\mu c/\mu g$ will deteriorate at a rate of $\simeq$2% year because of self-irradiation when stored in the cold in concentrations of $\simeq$1 μg/ml.[11,12] Even greater self-irradiation stability is exhibited by vitamin labelled with cobalt-57 and cobalt-58.[12]

CLINICAL APPLICATION

The earliest application of cobalt-labelled vitamin B_{12} led, fittingly, to simple and direct methods of diagnosis of pernicious anaemia, a disease for which vitamin B_{12} is a specific and life-saving treatment. Pernicious anaemia results essentially from the failure of the human stomach to secrete a substance called intrinsic factor. This factor is necessary for the oral absorption of vitamin B_{12}, which is of microbial origin and which is present in ingested food. Haematological diagnosis is a difficult and time-consuming procedure, depending as it does upon observations of the effect of doses of vitamin B_{12} on the blood picture and on changes therein. Radioactive vitamin B_{12}, however, permits a direct measurement of cyanocobalamin absorption[2] from observation of the (1) extent of faecal excretion, (2) extent of urinary excretion, (3) measurements of blood radioactivity, (4) external body scintillation counting over the liver area, and (5) by whole body counting. By these methods, the degree of oral absorption of vitamin B_{12}, and the effect of potent intrinsic factor preparations on oral absorption, are readily ascertained, and a judgement made as to whether absorption is normal or defective. By similar procedures the potency of intrinsic factor preparations employed for the treatment of pernicious anaemia can be evaluated, and the relative absorbability and retention of the several vitamin B_{12} analogues by animals and by man compared. These applications are based on measurements of the extent of vitamin transport from the gastro-intestinal tract, across the intestinal wall, into the blood stream and other tissue. The radioactive properties of the labelled vitamin make it possible to distinguish ingested vitamin in a medium which contains comparatively larger amounts of endogenous vitamin B_{12}.

Innumerable animal studies have revealed the pattern of distribution and excretion of vitamin B_{12} in animals and demonstrated the target organs and storage sites of the vitamin. A major storage site for the vitamin ingested by animals is the liver. The chief site of absorption from the gut appears to be the ileum, and the operation of an enterohepatic mechanism has been discovered. Turnover studies reveal the existence of several compartments or excretion forms of the vitamin.

ISOTOPE DILUTION ASSAYS

Radioactive vitamin B_{12} has been employed as an isotope dilution indicator to police the plant production of cyanocobalamin.[13] Assays[14,15,16] have been performed similarly of fermentation broths, sludge products, pharmaceutical preparations, oral grade solids and tissues, and crystalline vitamin B_{12}. In fact, the isotope dilution or "Radioisotope Tracer" method has been included in the U.S. Pharmacopoeia XV and the National Formulary XI as a standard cobalamin assay.[17]

The principle of the method and the conditions which must be satisfied for the proper application have been discussed elsewhere.[11] To a sample containing X μg of cyanocobalamin, one adds an amount Y μg of radioactive cyanocobalamin with a specific activity $S_0 = \frac{\text{A cpm}}{\text{Y}\,\mu\text{g}}$. Here, A cpm is the radioactivity of the tracer added in counts per minute on a suitable detection device. After treatment to ensure mixing of labelled and unlabelled vitamin, and isolation of a portion of the pure, or uniquely determined vitamin, one measures the radioactivity (B cpm) and quantity (Z μg) of a portion of the isolate. The specific activity of the isolate is obviously $S_f = \frac{B}{Z}$. The expressions by which X can be computed are

$$X = Y\left[\frac{S_0}{S_f} - 1\right] = Y\frac{S_0}{S_f} - Y = Z\frac{A}{B} - Y. \tag{1}$$

The ratio $\frac{A}{B}$ is the factor which corrects the quantity Z for inefficiency of isolation, and the term Y is subtracted from the total cyanocobalamin to correct for the quantity of radioactive indicator added initially. Specific activities of labelled vitamin are usually so high that the amount Y required for accurate radioactivity measurements is negligible compared to X. The above equations reduce accordingly to

$$X = Y\frac{S_0}{S_f} = Z\frac{A}{B}. \tag{2}$$

In the case of vitamin B_{12}, homogenisation of tracer with complex media, such as tissue, in which the vitamin may be retained within cellular matter and bound by biological components as proteins, is assured by treatment with acid nitrite, enzymes, and/or heat. Isolation is rather complicated, involving a variety of separation and purification procedures. A typical sequence of these steps applicable to the determination of total cobalamins in dog liver is enumerated below. Many modifications are permissible depending on the complexity of the matrix and the initial cobalamin content.

Isolation procedure for liver: total cobalamins

1. Homogenise 200 g of tissue with $\simeq$350 ml of water; add radioactive vitamin B_{12} and mix*; add $NaNO_2$ ($\simeq$5 mg/ml) and KCN ($\simeq$2 mg/ml)†.
2. Adjust to pH 4 with glacial acetic acid; boil 1 hr with stirring (caution: in hood).
3. Zinc defaecation: Cool and add 40 g of $ZnSO_4$ and sufficient 20% NaOH to yield a pH of 7·8–8·0. Filter.
4. Extract with 10 ml of cresol:CCl_4 (1:1); wash twice with 10 ml of H_2O.
5. Dilute the cresol:CCl_4 extract with 3 volumes of butanol:CCl_4 (1:4); extract into 10 ml of water.
6. Re-extract the aqueous phase with 5 ml of cresol:CCl_4 (1:1).
7. Repeat steps 5 and 6.
8. Wash the cresol:CCl_4 extract four times with 10 ml of 5*N* H_2SO_4 and twice with 20 ml of pH 9 phosphate buffer (40 g of Na_2HPO_4/1.) containing a trace of cyanide (0·001*N*).
9. Repeat steps 5 and 6.
10. Repeat step 5 extraction into 2 ml of H_2O.
11. Charge to chromatographic column (1 cm in diameter) containing (top to bottom) 2 g of alumina, 5 g of wet IRA 400 (OH cycle) and 5 g of wet IR120 (H cycle). Elute with water.
12. Collect the aqueous eluate when a pink colour appears. Total volume will be 5 ml. Determine the cyanocobalamin content (Z) spectrophotometrically at 361 mμ and its associated radioactivity (B cpm).

This treatment is capable of eliminating "red pigments" resembling cobalamins in structure but devoid of comparable biological and clinical activity.[16]

Because the amount of cobalamin in the isolate is determined spectrophotometrically from absorbancies at 361 mμ, $\left(A^{1\%}_{1\ \mathrm{cm}} = 207\right)$ and the efficiency of isolation $\frac{B}{A}$ is 30–50%, one needs a bare minimum of 50 μg/sample to give a reasonably accurate absorbancy in the final 3–5 ml of resin column eluate usually recovered. Because so large a sample is required, other tissues, which contained $\leqslant$0·5 μg/g, have not been assayed by the isotope dilution method. Blood plasma or serum, for example, contains the order of 0·3 mμg of cobalamin/ml, which is completely out of reach of this procedure. Fortunately, another approach to be discussed below makes it possible to analyse even this tissue concentration by the radioactive indicator method.

Results of the isotope dilution assay of a feed concentrate are shown in Table III. Two 100-g samples were analysed by a procedure modified from that described above for liver, by omission of the nitrate treatment and the initial introduction of an alcohol or water extraction procedure. The radioactive cyanocobalamin employed had a specific activity of $\simeq$ 60 μc/mg and the amount added was $\simeq$ 26 μg, which is not a negligible quantity, so that a correction for added tracer (Y) had to be applied. The average concentration was 2·6 μg/g or 1·2 mg/lb of concentrate which agreed

* Remove $\simeq$2–4 g of homogenate as a standard to determine A cpm.

† If only cyanocobalamin instead of total cobalamin is being sought, cyanide addition is omitted.

TABLE III—ISOTOPE DILUTION ASSAY FOR VITAMIN B_{12}

Sample size, *g*	100	100
Solvent	Water	Methanol
Amount vitamin B_{12}-^{60}Co (Y), μg	26	26
Vitamin B_{12} recovered (Z), μg	43	60
Recovered $\left(\frac{B}{A} \times 100\right)$, %	14·6	21·8
Vitamin B_{12} in sample (X)[a], μg	270	250

[a] $X = \dfrac{Z}{\left(\frac{B}{A}\right)} - Y.$

with other, less convenient, biological assays, such as the chick growth assay employed at the time.

Crystalline cyanocobalamin and hydroxocobalamin preparations are also most reliably assayed by the dilution procedure which is specific for cobalamins. For cyanocobalamin and total cobalamin, a reproducibility of ±3% has been estimated. Hydroxocobalamin preparations can be analysed as a difference between total cobalamin content (cyanide addition in step 1) and cyanocobalamin content (no cyanide addition). Typical results of total cobalamin assays for a series of pharmaceutical preparations, fermentation products and crystalline cobalamins are listed in Table IV. Isotope dilution analyses of the two pharmaceutical products are not influenced by the addition of inert coloured materials which do, however, increase the

TABLE IV—ASSAY OF VITAMIN B_{12} PREPARATIONS BY ISOTOPE DILUTION

Sample		Labelled claim	Assay results[a]			
			ID assay	*L. leichmannii* USP microbiological assay	Spectrophotometric assay	Chick growth assay
Pharmaceutical products[14]	Cobalamin concentrate	950–1350 μg/g	1076	1117	—	—
	Same plus 200 μg red pigments	Same plus 200 μg/g	1067	1186	—	—
	Liver injection	50 μg/ml	51·8	53·7	—	—
	Same plus red pigments	Same plus 16 μg/ml	52·7	59·9	—	—
Animal protein factor[15]	Sewage product	—	1·6	1·7	—	1·1
	Fermentation products	13·5 mg/lb	11·6	13·5	8·0	—
		113 mg/lb	<0·3	77	11·6	<4
		6·0 mg/lb	6·3	8·2	4·2	—
		3·0 mg/lb	3·0	4·2	1·8	2·6
Crystalline cobalamins	Cyanocobalamin	—	89·3%	—	87·2%	—
			89·7	—	91·2	—
			84·8	—	86·5	—
	Hydroxocobalamin	—	83·2	—	81·0	—
			78·7	—	81·2	—
			79·9	—	77·5	—

[a] Units the same as those listed under labelled claim.

L. leichmannii assay results. The analyses of vitamin B_{12} concentrates (*i.e.*, "animal protein factor") of fermentation origin emphasise the non specificity of microbial and spectrophotometric procedures as compared to the isotope dilution method, which is usually in good agreement with the chick-growth assay procedure. Agreement is also excellent for the crystalline cobalamin samples which contain 10–20% of volatiles.

The direct isotope dilution method has also been employed to demonstrate the thermal stability of hydroxocobalamin* in stabilised aqueous solution, buffered with acetate buffer and sodium chloride to pH 4·2 and containing $\simeq 1$ mg of hydroxocobalamin/ml. Extrapolation to room temperature of accelerated test data gathered at 40°, 75° and 121° indicated a half-life of 15–20 years, corresponding to a loss of $\nless 4\%$ of hydroxocobalamin/year.

REVERSE ISOTOPE DILUTION

The biochemist studying the mechanism of action or the degradation of a compound into metabolites frequently administers an isotopic modification and fractionates tissue or excreta into labelled components, the nature and quantity of which he seeks to ascertain. The chemist can apply the same technique to stability studies; and to facilitate recovery and assure identity at very low concentrations, he can add an excess of unlabelled modification as carrier before isolation. This is the reverse isotope dilution procedure; and in contrast to isotope dilution, it is not limited by the sensitivity of a spectrophotometric measurement but only by the detection sensitivity of the labelled cobalamin which, for cyanocobalamin containing radioactive cobalt, is in the picagram range. In the reverse isotope dilution assay method one adds the desired amount of the radioactive vitamin $B_{12}\left(X_0\ \mu g;\ A\ \text{cpm};\ S_0 = \frac{A}{X_0}\right)$ to the matrix in question. This matrix might be simply an aqueous solution if thermal or radiochemical stability[11] of solutions is concerned or, as has been already reported, cereals or capsules containing biological concentrates.[11,18] Degradation studies in animals receiving labelled vitamin are also cases in point.

At any subsequent time of interest, a large excess (Y mg) of carrier cobalamin is added, and isolation undertaken with recovery of an isolate containing Z mg of cobalamin and B cpm $\left(i.e.,\ S_f = \frac{B}{Z}\right)$. The value of Z is again measured spectrophotometrically. If the actual amount of residual vitamin B_{12} is X μg, then one may say

$$X = Y\left[\frac{1}{\frac{S_0}{S_f} - 1}\right] \text{ or } X = Y\frac{S_f}{S_0} \text{ because } So \gg S_f.$$

Accordingly, the percentage of cohalamin left is

$$\frac{X}{X_0} \times 100 = \left[\frac{Y}{Z} \times B\right] \times \frac{100}{A} \tag{3}$$

Here, $\frac{Y}{Z}$ is the spectrophotometric factor correcting for incomplete recovery of

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* Experiments performed by Miss Beate Feller and Messrs. J. Carr, E. J. Hanus and J. Kanora of these Laboratories.

B cpm, $\left[\frac{Y}{Z}\times B\right]$ is the actual radioactivity in cpm recovered with the X μg of cobalamin, and $\frac{X}{X_0}\times 100$ is the percentage of initial radioactivity (A) still recoverable as cobalamin. This method is independent of the presence of endogenous cobalamins.

An obvious use of this approach is for the establishment of the radiochemical purity and authenticity of a labelled compound. This is part of the armoury of methods which the radiochemist employs to prove the suitability of labelled materials. An application of more general analytical relevance is illustrated by the measurement of the radiochemical[11] stability of vitamin B_{12} in aqueous solution employing ^{60}Co-labelled vitamin. Thermal stability has also been investigated. A stabilisation study* of cyanocobalamin in the presence of ascorbic acid is reported in Table V.

TABLE V—STABILISATION OF VITAMIN B_{12} IN AQUEOUS SOLUTION CONTAINING ASCORBIC ACID (ROOM TEMPERATURE STORAGE)

Agent[b]		Composition[b]		B_{12} left, %			
No.	Concn., *mg/ml*	B_{12}, *µg/ml*	AA, *mg/ml*	0	2 months	6·5 months	10·5 months
IFC-1	2	0·25	12·5	—	—	85	87
IFC-1	6	0·83	12·5	96	92	97	—
IFC-2	0·6	0·25	12·5	—	—	80	—
IFC-2	2	0·83	12·5	98	85	80	—
IFC-3	2	0·83	12·5	98	64	52	—
IFC-3	10	0·83	12·5	107	80	106	—
IFC-6	2	0·83	12·5	97	86	75	—
IFC-6	10	0·83	12·5	98	87	94	—
IFC-7	2	0·83	12·5	99	95	63	—
IFC-7	10	0·83	12·5	100	81	71	—
IFC-8	2	0·83	12·5	94	88	43	—
IFC-8	10	0·83	12·5	101	87	92	—
Agar	5	0·25	12·5	—	—	70	—
Sorbitol	420	0·83	12·5	99	57	34	—
Bovine albumin	10	0·25	12·5	—	—	63	—
Liver fraction	8·2	0·25	12·5	—	—	68	—
Gelatin	2–10	1·14	11·5	—	8–5[a]	—	—
Cerula-plasmin	2–6	1·14	11·5	—	1–9[a]	—	—
Yeast nucleic acid	10	0·25	12·5	—	—	65	9
None	—	0·25	12·5	—	—	29	—

[a] ≃ 3 months.
[b] IF = intrinsic factor; AA = ascorbic acid.

Stock aqueous solutions were prepared from protective agent, ascorbic acid and cyanocobalamin-^{60}Co, and analyses by reverse isotope dilution performed initially and after ≌3, 6·5 and 10·5 months. Protective agents assayed included intrinsic factor concentrates, agar, sorbitol and proteins. Stabilisation was suspected in view of

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* Experiments performed by Messrs. H. T. Meriwether and P. E. Gethard of these Laboratories.

numerous reports of enhanced oral absorption of the vitamin ingested simultaneously with certain of these materials. Because clear solutions were involved, it was not necessary to apply that part of the isolation procedure designed to eliminate tissue components. Estimates based on spectral changes are uncertain because of the lack of knowledge of degradation products and their spectra. The dilution procedure is unequivocal in that pure cobalamin is isolated. It is also performed more expeditiously than a microbiological assay. Given the rapid degradation of vitamin B_{12} in the presence of ascorbic acid, it is seen from Table V that the vitamin is indeed much stabilised by several of the intrinsic factor preparations. Neither sorbitol nor the proteins were effective.

The fate of administered cyanocobalamin retained in animal tissue has also been studied by the reverse isotope dilution method. Thus, practically all of the radioactivity resident in the liver of dogs receiving 3·6 or 14·3 μg of vitamin B_{12}-^{60}Co by the intravenous route and examined 5–71 days after dosing, were found to be recoverable as a cobalamin.[19] The isolation procedure described above was applied to these liver specimens. This being the case, the resident cobalt-60 radioactivity could be assumed to represent vitamin B_{12}-^{60}Co, which could thus serve as a resident indicator for determining the vitamin B_{12} content of the liver specimens by the direct isotope dilution method. This was confirmed by direct isolation (without addition of carrier) of total cobalamin from 100 to 200-g samples of tissue and measuring its activity (B cpm) and quantity (Z) in the isolate. The value of the initial radioactivity (A cpm) was obtained by direct measurement of the tissue radioactivity. The cobalamin content of dog livers could then be calculated from equation (2). These values were confirmed simultaneously by the addition of high specific activity vitamin B_{12}-^{57}Co tracer prior to isolation. The actual isotope dilution analysis thus constituted a "double labelling" tracer experiment in which cobalt-60 and cobalt-57 were determined simultaneously in a gamma-ray scintillation spectrometer. Results are reported in Table VI which show that resident cobalt-60 radioactivity is recoverable quantitatively as a cobalamin, and the cobalamin could serve as an indigenous tracer for vitamin B_{12} because it yielded essentially the same values for the vitamin B_{12} content of dog liver as did exogenous vitamin B_{12}-^{57}Co.

Although retained as an intact cobalamin, the administered cyanocobalamin does

TABLE VI.—VITAMIN B_{12} CONTENT OF DOG LIVERS

Dog	Cobalamins, %	Cobalamin ($\mu g/g$) by isotope dilution	
		^{60}Co	^{57}Co
282	103; 100	0·10 0·06	0·08 0·07
274	98; 104	0·14	0·14
276	97; 98	—	—
328	95	0·28	0·24
320	95	—	—

undergo considerable conversion to the hydroxo analogue. This was shown by the reverse isotope dilution method employing the proteolytic enzyme papain instead of nitrous acid to liberate bound vitamin B_{12} from protein and other tissue components, and by using both cyanocobalamin and hydroxocobalamin as carriers. In this study,[20] 2·4 μg of oral vitamin B_{12}-^{57}Co and $\simeq$14 μg of intravenous vitamin B_{12}-^{60}Co were administered in divided doses, and tissues examined 4 weeks after the last dose. It appears from Table VII that, regardless of the mode of administration, most of the radioactivity was recoverable as hydroxocobalamin, and that only 7–25% was retained as intact cyanocobalamin. This is consistent with the observation that hydroxocobalamin predominates among the natural sources of vitamin B_{12} activity.

TABLE VII.—REVERSE ISOTOPE DILUTION ASSAY OF DOG LIVERS (PAPAIN TREATMENT)

Dog	Carriers	Boiled, *min*	Recovered as			
			Cyanocobalamin, %		Hydroxocobalamin, %	
			^{57}Co	^{60}Co	^{57}Co	^{60}Co
1	Cyano + hydroxo	15[a]	6·7	7·4	101	108
		60[a]	19·7	21·4	66·6	66·4
2	Cyano	15	9·6	10·8	—	—
	Cyano	15	16·5	13·8	—	—
	Cyano + hydroxo	15	6·6	6·2	100	100
		60[a]	25·2	26·1	64·5	60·5
		60	17·7	17·1	70·4	69·2
		120	22·8	21·7	62·1	61·5
	Hydroxo	60	—	—	100	105

[a] These isolates were further purified by chromatography on paper, elution, solvent extraction and ion-exchange resins. Results were essentially the same as in the standard procedure.

SATURATION ANALYSIS

The interaction between vitamin B_{12} and micro organisms, blood serum, intrinsic factor and other substances of biological importance has received intensive study because of the possible diagnostic significance and to gain an insight into the mechanism of action of the vitamin. This "binding power" for vitamin B_{12} has been employed, among other uses, as a qualitative indication of the potency of intrinsic factor (IF) preparations, and to guide the concentration and isolation of this biological material from animal intestinal sources.[21] The binding power (BP) is measured most easily if a radioactive vitamin is employed. In principle, one only needs to incubate suitable amounts of intrinsic factor concentrate (IFC) with an excess of labelled cyanocobalamin and, after a predetermined time, remove free vitamin by dialysis,[22] adsorption, chromatography or by electrophoresis. If the intrinsic factor is recovered quantitatively, as in the dialysis procedure where it remains in the dialysis sac employed, its radioactivity as measured by scintillation counting indicates the weight of vitamin B_{12} retained by the IF present, and the weight of vitamin/unit weight of binder (*i.e.*, BP) follows. Alternatively, the excess radioactive vitamin B_{12} removed by the inert adsorbent could be measured and the bound vitamin deduced by difference. A typical set of data[23] is illustrated in Table VIII, which shows the amount (mg) of a given intrinsic factor preparation added to 15 ml of solution containing a total of 624 mμg of cyanocobalamin-^{60}Co before dialysis, the percentage of vitamin retained by the intrinsic factor concentrate after incubation at room temperature for 1 hr and dialysis in Nojax casing against running tap water for 22 hr, and the ratio of the retained vitamin (mμg) to the weight (mg) of binder. Up to 0·928 mg of intrinsic factor concentrate, a constant average binding power of 675 mμg/mg is obtained because the binding capacity of the IFC is saturated. Beyond this point, which just corresponds to the retention of 100% of the labelled vitamin, the vitamin excess is exhausted and progressively lower B_{12}/IF ratios are obtained.

TABLE VIII—BINDING OF VITAMIN B_{12} BY INTRINSIC FACTOR CONCENTRATE (VITAMIN ADDED: 624 mμg)

Wt. IF, *mg*	B_{12} bound, %	BP, *mμg/mg*	Wt. IF, *mg*	B_{12} bound, %	BP, *mμg/mg*
0·055	5·7	650	0·764	84·0	686
0·218	23·1	660	0·819	89·3	681
0·328	35·2	669	0·874	94·2	672
0·437	48·4	689	0·928	99·5	669
0·546	56·8	650	1·09	99·6	570
0·655	73·7	701	1·64	97	370
0·710	79·5	699	2·18	97	280

At higher concentrations of vitamin, the percentage of total vitamin bound/given weight of IF would be lower because its binding power is fixed and its capacity already saturated. Clearly, therefore, the addition of extraneous vitamin B_{12} to the system represented in Table VIII would lower the percentage of vitamin B_{12} bound, and the radioactivity retained would be less than the figures shown in Table VIII. This, in effect, would constitute an isotope dilution assay without separation of the isotopic mixture for measurement. This would be valid if no extraneous components in the medium interfere with the binding of vitamin B_{12}; then the IF serves both to isolate pure or uniquely distinguished radioactive vitamin and to permit facile measurement of final specific activity. This approach to the measurement of small amounts of vitamin B_{12} was proposed[24] for the assay of urine and applied[25] to the measurement of the capacity of gastric juice to bind the vitamin. The adsorbent there was resting *L. leichmannii*[24] cells; the proposal was never actively pursued, presumably because of the difficulty of cultivating a cellular mass of uniform and reproducible binding capacity.

This principle* has since been applied to the micro estimation of fluoride[26] and, under the designation of "saturation analysis", to the analysis of biological media for insulin,[27] thyroxine[28] and recently, again vitamin B_{12}.[29,30,31] The vitamin B_{12} adsorbents utilised are, however, not micro organisms but hog intrinsic factor concentrate,[30]

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* A similar principle was employed[32] to determine the solubility of lead sulphate in aqueous solutions containing large excesses of sodium sulphate and in alcohol-water mixtures. The indicator utilised was the lead isotope ThB(^{212}Pb) and the adsorbent was lead sulphate of predetermined specific surface.

which is a proteinaceous material, or other binding protein as is supplied in a "standard" serum[31] or plasma[29] specimen. In all of these proposals, a specimen of urine, plasma or serum of unknown vitamin B_{12} content is heated to liberate its vitamin B_{12} burden, and incubated with a fixed amount of radioactive vitamin B_{12}-(^{57}Co or -^{60}Co) and a standardised vitamin B_{12} binder. After incubation for a suitable period, the sequestered radioactivity is determined either (1) by dialysis[29] to remove excess ("free") vitamin and measurement of residual ("bound") radioactivity, (2) by removal of free vitamin by adsorption on charcoal[31] and measurement of same, or (3) by removal of bound vitamin by precipitation of the IF-vitamin B_{12} complex by the Somogyi method,[30] and measurement of the free vitamin left in the filtrate. Because the quantity of the initial radioactive vitamin employed is known, one can always deduce the relative amounts of free and bound vitamin, and the ratios of these quantities, and from this measurement deduce the vitamin B_{12} content of the urine or plasma sample.

TABLE IX—COMPARISON OF VITAMIN B_{12} ASSAY METHODS

	Sample	Investigator[a]	Vitamin B_{12}, *mμg/ml*	
			Radiometric	Microbiological
Urine	Infectious hepatitis	G, S & M	0·25–16	0·10–12
Serum	Normals	B & E	0·33–0·84	0·27–1·2
Serum	Normals	R	0·10–0·33	—
Serum	Normals	B, S & M	0·50–0·60	—
Serum	Macrocytic anaemia	B & E	0·01–0·074	—
Serum	Macrocytic anaemia	R	0–0·072	—
Serum	Macrocytic anaemia (after treatment with vitamin B_{12})	G, S & M	1·0	1·2
Serum	Myeloid leukaemia	B & K	9·0	—
Serum	Myeloid leukaemia	G, S & M	2·5	3·5
Serum	Infectious hepatitis	G, S & M	2·5–4·0	2·0–4·8
Serum	Liver cirrhosis	G, S & M	1·5	1·6

[a] Grossowicz, Sulitzeanu and Merzbach; Barakat and Ekins; Rothenburg.

It has been customary among investigators to construct a calibration curve relating exogenous crystalline vitamin B_{12} concentration (1) with free radioactive vitamin,[31] or (2) with the ratio of free to bound[29] radioactive vitamin or the inverse ratio,[30] and reading the vitamin B_{12} concentration of an unknown from such a calibration curve. A plot of Free/Bound radioactive vitamin *vs.* vitamin B_{12} concentration is perhaps most convenient because it is linear. The identification of saturation analysis as an isotope dilution procedure, where the adsorbent serves the dual function of isolation and facilitating the determination of final specific activity, was recognised by one group of investigators[29] whose expression for vitamin B_{12} concentration of an unknown is: $B_{12}\ \mathrm{m\mu g/ml} = \frac{C_a}{V}\left[\frac{B}{C_r} - \frac{1}{S}\right]$, where V = sample volume; C_a = cpm added; C_r = cpm in aliquot dialysed; B = mμg of vitamin B_{12} interpolated from the linear calibration curve; and S = specific activity of the radioactive vitamin B_{12} in cpm/mμg. Rewriting with the notation employed above in an earlier section, we have $V \times B_{12} = X$; $C_a = A$ cpm; $S = S_0$; $B = Z$; and $C_r = B$ cpm, so that the preceding expression becomes $X = \frac{A}{B} Z - Y$, a standard isotope dilution equation.

This "saturation" variant of the isotope dilution method for vitamin B_{12} yields results in excellent agreement with those of microbiological assays for urine and serum, and has the advantages of being much more rapid and probably more reproducible. A comparison of both methods, and of the radiometric method as applied by its several protagonists, is shown in Table IX. This version of the isotope dilution method is significant as an extension of the vitamin B_{12} assay to physiological concentrations. Hitherto, one had been limited by the detection sensitivity of the spectrophotometric method to levels above approximately 50 μg/sample. This quantity is far beyond that which is readily available in samples of tissue and body fluids. The greatly increased detection sensitivity for vitamin B_{12} attainable with the adsorption method permits the analysis of extremely low levels of vitamin present in natural media, and opens up a whole area of applicability for the isotope dilution method.

Zusammenfassung—Radioaktives Vitamin B_{12} wurde als analytisches Hilfsmittel, als biochemischer Tracer und als diagnostisches Agens eingesetzt. Von den verschiedenen beschriebenen markierten Verbindungen sind nur die mit isotopem Kobalt markierten in physiologischen Dosierungen von Nutzen. Wegen der hohen spezifischen Aktivitäten von 1-200 μc/μg lassen sich Nachweisgrenzen im Picogrammbereich mit kobaltmarkiertem Vitamin B_{12} realisieren. Klinische Anwendungen, wie diagnostische Tests auf perniciöse Anämie beim Menschen, sind gewissermaßen analytische Vorgänge, die Messungen des Vitamin B_{12}-Transports erfordern. Von deutlicher analytischem Charakter ist die Anwendung der Isotopenverdünnungsmethode auf pharmazeutische Präparate, Nahrungskonzentrate, Abfall- und Gärungsprodukte und kristalline Cobalamine. Die Beständigkeit von Hydroxocobalamin in stabilisierter wäßriger Lösung bei p_H 4,2 wurde auf diese Weise gezeigt. Die umgekehrte Isotopenverdünnungsmethode war bei der Erleichterung von Stabilitäts- undAbbauuntersuchungen ebenfalls sehr nützlich. Auf diese Weise wurde die quantitative Gewinnung unveränderten Cyanocobalamins aus Getreide und aus biologische Konzentrate enthaltenden Kapseln gezeigt. Umgekehrt wurde Umwandlung von Cyanocobalamin zu Hydroxocobalamin in der Leber von mit markiertem Vitamin gefütterten Hunden gefunden. Eine umfangreiche Untersuchung über Agentien zur Stabilisierung von Vitamin B_{12} in ascorbinsäurehaltigen Lösungen wurde mit Hilfe des umgekehrten Isotopenverdünnungsverfahrens durchgeführt. Die Empfindlichkeit der Isotopenverdünnungsmethode wurde in Richtung auf physiologische Mengen stark ausgedehnt durch Anwendung der "Sättigungsanalyse", eine Erweiterung der Messung der Bindungskraft, die auf "intrinsic factor-"Konzentrate und auf tierische Gewebe einschließlich Serum oder Plasma angewandt wurde.

Résumé—La vitamine B_{12} radioactive a été employée dans un but analytique, comme traceur biologique et comme agent de diagnostic. Des différentes molécules marquées, seules celles marquées avec des isotopes du cobalt sont utiles au niveau des doses physiologiques. A cause des hautes activités spécifiques de (1–200) μc/μg, la sensibilité de la détection dans la région du picagramme utilise de la vitamine B_{12} marquée au cobalt. Des applications cliniques, y compris les diagnostics de l'anémie pernicieuse chez l'homme, sont, en un sens, des moyens analytiques comprenant des mesures du transport de la vitamine B_{12}. D'un caractère analytique plus direct est l'application

de la méthode de dilution isotopique aux préparations pharmaceutiques, concentrés alimentaires, produits de dégradation et de fermentation et aux cobaltamines cristallisées. On a montré par cette méthode la stabilité de l'hydroxocobaltamine en solution aqueuse tamponnée ($pH = 4,2$). La méthode de dilution isotopique en retour est aussi très utile pour faciliter les études de stabilité et de dégradation. On a montré par cette méthode que, dans les céréales et dans des capsules contenant des concentrés biologiques, on retrouvait la même quantité de cyanocobaltamine n'ayant subi aucune transformation. Au contraire, la cyanocobaltamine se transforme en hydroxocobaltamine dans le foie des chiens recevant de la vitamine marquée. Toujours par cette méthode on a peu effectuer une étude complète des agents protecteurs pour stabiliser la vitamine B_{12} dans des solutions contenant de l'acide ascorbique. La sensibilité de la dilution isotopique a été grandement accrue vers les niveaux physiologiques par l'application de "l'analyse de saturation", une extension de la mesure du pouvoir de liaison appliquée au facteur intrinsèque des concentrés et aux tissus animaux contenant du sérum ou du plasma.

REFERENCES

[1] C. Rosenblum, *2nd Europ. Symposion über Vitamin B_{12} u. Intrinsic Factor, Hamburg* 1961, Enke, Stuttgart, 1962, p. 306.

[2] R. Gräsbeck, *ibid*, p. 318.

[3] A. F. Wagner and K. Folkers in *Medicinal Chemistry*. Interscience Publishers, New York, 1960, p. 257.

[4] E. L. Smith, *Vitamin B_{12}*. Methuen, London and John Wiley, New York, 1960.

[5] D. Hendlin and M. L. Ruger, *Science*, 1960, **111**, 541.

[6] G. E. Boxer, J. C. Rickards, C. Rosenblum and D. T. Woodbury, *Arch. Biochem.*, 1951, **30**, 470.

[7] E. L. Smith, S. Ball and D. M. Ireland, *Biochem. J.*, 1952, **52**, 395.

[8] R. N. Boos, C. Rosenblum, and D. T. Woodbury, *J. Amer. Chem. Soc.*, 1951, **73**, 5446.

[9] L. Chaiet, C. Rosenblum and D. T. Woodbury, *Science*, 1950, **111**, 601.

[10] J. L. Sommerville, ed., *The Isotope Index* 1962. Sci. Equipment Co., Indianapolis, 1962, p. 142.

[11] C. Rosenblum, *Analyt. Chem.*, 1957, **29**, 1740.

[12] C. Rosenblum, *2nd Europ. Symposium über Vitamin B_{12} u. Intrinsic Factor, Hamburg*, 1961, Enke, Stuttgart, 1962, p. 294.

[13] E. L. Smith, *Radioisotope Techniques*. H. M. Stationery Office, 1953, **1**, 281.

[14] F. A. Bacher, A. E. Boley and C. E. Shonk, *Analyt. Chem.*, 1954, **26**, 1146.

[15] L. Chaiet, T. Miller and A. E. Boley, *J. Agric. Food Chem.*, 1954, **2**, 784.

[16] C. F. Bruening, J. D. Neuss, P. Numerof and O. L. Kline, *J. Amer. Pharmaceut. Assoc. Sci. Ed.*, 1957, **46**, 66.

[17] *U.S. Pharmacopoeia*, *XV*, First Supplement, 1956, p. 1; National Formulary XI. 1960, p. 419.

[18] C. Rosenblum and D. T. Woodbury, *J. Amer. Pharmaceut. Assoc. Sci. Ed.*, 1952, **41**, 368.

[19] C. Rosenblum, D. A. Willigan, H. T. Meriwether and E. P. Cronkite, *Proc. Soc. Exp. Biol. Med.*, 1960, **105**, 142.

[20] C. Rosenblum, P. J. Reizenstein, E. P. Cronkite and H. T. Meriwether, *ibid.*, 1963, **112**, 262.

[21] P. R. Burkholder, *Arch. Biochem. Biophys.*, 1952, **39**, 322.

[22] O. D. Bird and B. Hoevet, *J. Biol. Chem.*, 1951, **190**, 181.

[23] C. Rosenblum, D. T. Woodbury and E. H. Reisner, Jr., *Proceedings of the 2nd Oxford Radioisotope Conference, July* 1954. Butterworth, London, 1954, Vol. I, p. 287.

[24] R. L. Davis and B. F. Chow, *Science*, 1952, **115**, 351.

[25] R. S. Yamamoto and B. F. Chow, *J. Lab. Clin. Med.*, 1954, **43**, 316.

[26] J. N. Kudahl, J. H. Fremlin and J. L. Hardwick, *Radioisotopes in the Physical Sciences and Industry*, VII, Int. Atomic Energy Agency, Vienna, 1962, p. 317.

[27] S. A. Berson, R. S. Yalow, A. Bauman, M. A. Rothschild and K. Newerly, *J. Clin. Invest.*, 1956, **35**, 170.

[28] R. P. Ekins, *Clinica Chim. Acta.*, 1960, **5**, 453.

[29] R. M. Barakat and R. P. Ekins, *Lancet*, 1961, VII, 25.

[30] S. P. Rothenberg, *Proc. Soc. Exp. Biol. Med.*, 1961, **108**, 45.

[31] N. Grossowicz, D. Sulitzeanu and D. Merzbach, *ibid.*, 1962, **109**, 604.

[32] C. Rosenblum, *Chem. Rev.*, 1935, **16**, 99.

Talanta, 1964, Vol. 11, pp. 271 to 281. Pergamon Press Ltd. Printed in Northern Ireland

SOME PHYSICAL PROPERTIES OF HIGHLY PURIFIED BROMINE

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Summary—The electrical conductivity of very pure bromine is lower than that given in most of the earlier literature, and the surface tension is slightly higher. In the liquid range, these properties can be expressed by the equations $\log k = -11{\cdot}372 + 0{\cdot}0128t$ and $\gamma = 45{\cdot}5 - 0{\cdot}182t$, where k is in ohm^{-1}.cm^{-1}, γ in dyne . cm^{-1} and t in °C. Data on the thermal conductivity of the liquid are given for the first time.

INTRODUCTION

AMONG the continuing interests of this laboratory is one involving the properties and applications of bromine and its compounds. Through the years, elemental bromine has become available commercially with ever-increasing purity, until the 99·98–99·99% products on the market today rival the especially purified materials used for properties measurements some generations ago. Much of the improvement in the commercial product derives from better methods of fractionation and other treatments to remove organic substances and chlorine, recognition of the need for eliminating moisture and acidity to minimise corrosion problems, and the development of improved analytical methods for detecting impurities. Infrared analysis, for example, can reveal the presence of a few ppm of moisture as well as of chloroform and other partially halogenated hydrocarbons. Wagner[19] has recently pointed out that pure bromine is transparent throughout the normal infrared region, a fact which had been known in the industry for quite a few years. The difficulty of removing the last traces of organic substances by permanganate or chromic acid oxidation had not been realised originally. Thermal oxidation processes have been found in this laboratory to be more effective. One such process has been described by Codell and Norwitz.[4]

With high-purity bromine available as a starting material, it appeared desirable to make new determinations of some of the physical properties of this element. The present paper deals with measurements of the electrical conductivity of liquid and solid bromine, and of the thermal conductivity and surface tension of liquid bromine.

I—ELECTRICAL CONDUCTIVITY

Previous determinations of the specific conductance of bromine have given results as shown in Table I (*cf.* Sharpe[18]).

The data are concordant in that they all indicate a very high resistance of bromine, but discrepancies are evident. It should be noted that Exner's value, reported in 1882, was necessarily obtained with equipment inferior to that available later, and that Moessen and Kraus in their work were concerned primarliy with bromine solutions rather than with a fundamental value for pure bromine. The conductivity of solid bromine has been reported by Rabinowitsch[14] as 8×10^{-12} at $-18{\cdot}5°$ and $4{\cdot}5 \times 10^{-11}$ at $-9°$.

TABLE I.—ELECTRICAL CONDUCTIVITY OF LIQUID BROMINE

Temp., °*C*	Spec. cond. (K), *mhos. cm*$^{-1}$	Reported by
-9^{a}	$5{\cdot}14 \times 10^{-10}$	Rabinowitsch[14]
-6	$5{\cdot}50 \times 10^{-10}$	Rabinowitsch[14]
$-5{\cdot}5$	$7{\cdot}94 \times 10^{-14}$	Exner[5]
0	$8{\cdot}63 \times 10^{-14}$	Exner[5]
0	$9{\cdot}6 \times 10^{-10}$	Anderson[2]
0	$6{\cdot}32 \times 10^{-10}$	Rabinowitsch[14]
15·5	$8{\cdot}95 \times 10^{-10}$	Rabinowitsch[14]
17·2	$1{\cdot}21 \times 10^{-13}$	Exner[5]
18	$1{\cdot}6 \times 10^{-9}$	Finkelstein[7]
25	$1{\cdot}12 \times 10^{-9}$	Rabinowitsch[14]
25	1 to 6×10^{-10}	Moessen and Kraus[12]
38·5	$2{\cdot}5 \times 10^{-13}$	Exner[5]

[a] Supercooled

EXPERIMENTAL

Purification of bromine

A procedure combining that of Codell and Norwitz[4] with that of Hildenbrand, Kramer, MacDonald and Stull[8] was employed. High-purity commercial bromine was vapourised and passed with oxygen through a quartz tube at 900°. The condensed bromine was allowed to stand overnight with about 10% of its weight of previously fused caesium bromide (to remove chlorine), then was distilled. Traces of hydrochloric acid, hydrobromic acid, carbon dioxide and water were removed by repeated vacuum distillations back and forth through drying tubes containing alternate layers of ignited magnesium oxide and barium oxide, in a closed system. The product was finally distilled under its own vapour pressure into the evacuated and cooled conductivity cell. Although no freezing-point data were obtained, the purity should be slightly better than that of Hildenbrand *et al.* Their data had indicated an impurity content of less than 0·001 mole per cent, but the presence of 10–15 ppm of chloroform was subsequently found by infrared analysis.

Apparatus

The conductivity cell consisted of a Pyrex chamber of about 150-ml capacity, having near the centre two parallel square tungsten electrodes 2·6 cm on a side and a little less than 0·5 mm apart. Electrical leads were also of tungsten, brought in from opposite sides through Pyrex tubes. The cell constant as determined at audio frequency with $0{\cdot}01M$ potassium chloride solution was $5{\cdot}92 \times 10^{-3}$.

Resistance was measured with a megohmmeter of a type similar to one described by Prinz,[13] loaned by V. J. Caldecourt. This had a feedback circuit yielding a linear current output proportional to the unknown resistance. The current was recorded by a Sargent MR recorder. The system was calibrated against a nominal $100M\Omega$ resistor, which in turn had been standardised in a Wheatstone bridge circuit against precision resistors of smaller magnitude.

Temperatures above 10° were regulated to within 0·01° in a bath of the usual type. For lower temperatures it was necessary to add dry ice periodically for cooling, and the constancy during reading intervals was only to about 0·1°. Transformer oil was used as a bath liquid with suitable insulating properties.

Procedure

The leads from the electrodes were kept short-circuited except for the 0·5-min periods of measurement. After each recording the polarity of the leads was reversed to lessen polarisation effects. The period between recordings was at least 5 min. In each run the applied d.c. voltage was small, about 5 V. Because the resistance of the system was found to increase with time, indicating polarisation, an extrapolation to zero time was made and taken as the true value of the resistance. A typical run is illustrated in Fig. 1, showing the extrapolation. At least four runs were made at each temperature.

The conductivity of solid bromine was obtained in the same equipment after lowering the loaded cell into a dry ice-trichlorethylene bath at a rate of 5 mm/hr. The measurement and extrapolation were made in the same way as for the liquid.

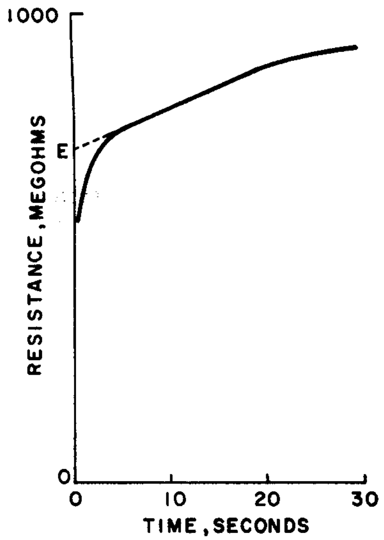

FIG. 1.—Change of resistance with time

RESULTS

Averaged values of the data obtained are presented in Table II. Generally, the individual runs at a given temperature yielded values agreeing within 3–5%. The conductances are estimated to be precise to 5% for the liquid and to 10% for the solid. The data are shown in a semi-log plot in Fig. 2. Over the linear range (liquid), the conductance can be represented by the equation:

$$\log k = -11{\cdot}372 + 0{\cdot}0128t$$

where k is in ohm^{-1}.cm^{-1}. and t is in °C.

TABLE II.—ELECTRICAL CONDUCTIVITY OF SOLID AND LIQUID BROMINE

Temp., °C	Resistance in cell, *MΩ*	Spec. cond. (K), *mhos. cm*$^{-1}$
−20·0 (solid)	21,250	$2{\cdot}8 \times 10^{-13}$
−15·0	16,350	$3{\cdot}6 \times 10^{-13}$
−10·0	11,050	$5{\cdot}35 \times 10^{-13}$
−7·3	7,320	$8{\cdot}1 \times 10^{-13}$
−7·0 (liquid)	1,800	$3{\cdot}3 \times 10^{-12}$
−5·0	1,610	$3{\cdot}7 \times 10^{-12}$
0·0	1,390	$4{\cdot}25 \times 10^{-12}$
5·0	1,210	$4{\cdot}90 \times 10^{-12}$
10·0	992	$5{\cdot}97 \times 10^{-12}$
15·0	888	$6{\cdot}67 \times 10^{-12}$
20·0	753	$7{\cdot}86 \times 10^{-12}$
25·0	651	$9{\cdot}10 \times 10^{-12}$
30·0	586	$1{\cdot}01 \times 10^{-11}$
35·0	497	$1{\cdot}19 \times 10^{-11}$
40·0	439	$1{\cdot}35 \times 10^{-11}$
45·0	369	$1{\cdot}60 \times 10^{-11}$
50·0	321	$1{\cdot}84 \times 10^{-11}$

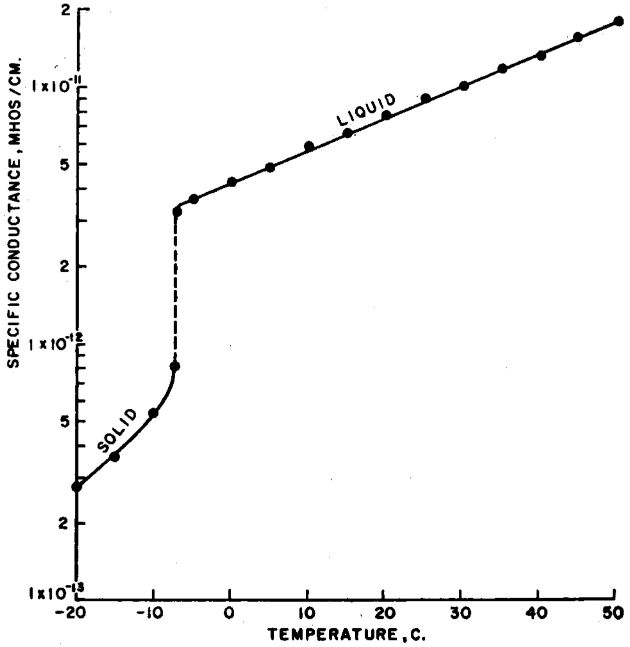

FIG. 2.—Electrical conductivity of bromine.

DISCUSSION

Tungsten rather than platinum was chosen for the electrodes because of the observation that on prolonged contact with bromine, platinum became coated with a thin layer of a brownish-yellow substance which upon solution in water would yield a spot test for platinum.[2,6] Tungsten remained unchanged throughout the experiments, though considerably later after standing in moist air, the electrodes were found to have acquired an olive-green coating. The inertness of tungsten towards bromine was also evidenced by potentiometric measurements in a bromine-bromide system. A tungsten electrode exhibited a stable and reproducible potential, positive to that of a silver or magnesium electrode but identical with that of a tantalum electrode in the same system.

Ideally, the conductivity should be measured at audio frequency. However, with a resistance of about 1000 $M\Omega$ any small capacitance would short-circuit the input, making a.c. measurement exceedingly difficult. Therefore d.c. measurements were used here as well as in most of the work previously cited. Moessen and Kraus[12] used an a.c. method.

While polarisation still existed in our experiments, it was minimised by the use of a low d.c. voltage, brief recording time and short-circuiting between recordings. The reproducibility of the extrapolated values and their independence of the polarity of the electrodes indicate that polarisation had not caused any permanent changes in the system.

It is of interest to note the course of polarisation over longer recording periods, similar to what was found by Anderson.[2] Curve I of Fig. 3 was obtained after the electrodes had been shorted for a long time. The resistance slowly rose to a maximum, then tapered off. Curve II was obtained immediately after I and with the polarity changed. The resistance rapidly rose to a maximum A, dropped to a minimum B and finally rose again to a nearly level maximum C. Additional recordings after immediate changes of polarity were similar in shape to curve II, except that the resistances were shifted to lower values. Anderson's curves also showed a minimum in resistance (or rather a maximum in current in her paper), which was taken as the correct value. Separate similar experiments here showed that if our minimum had been considered the correct value according to Anderson, it would be within 10 to 20% of the extrapolated value E of Fig. 1. The extrapolated value was more reproducible, however, and hence was chosen as the one to be reported.

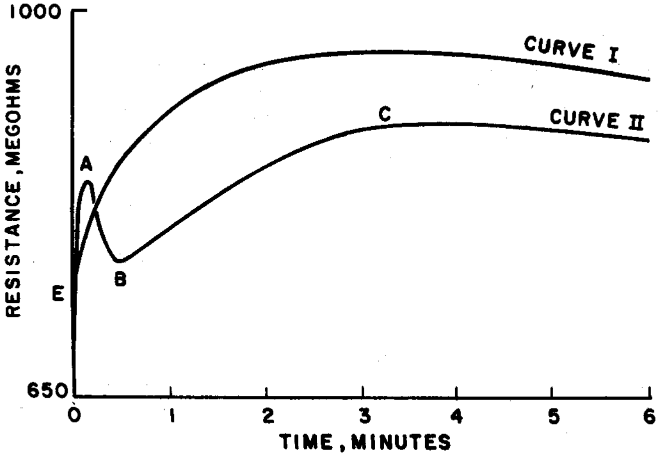

FIG. 3.—Effect of polarisation: Curve I—Resistance after prolonged shorting; Curve II—Resistance after passage of current and change of polarity.

Compared with the findings of other workers, except Exner, the present values are about two orders of magnitude smaller in specific conductance. This is attributed mainly to more complete removal of impurities, especially moisture, because a value more comparable with those of other workers ($1{\cdot}8 \times 10^{-10}$ at 25°) was observed in using high-quality commercial bromine without additional purification. Furthermore, the conductance of a purified sample continued to decrease with more passes through the purifying columns until about the tenth passage. On the other hand, Exner's values were about one order of magnitude smaller than ours. This may be fortuitous, in view of the fact that he used bromine without stated exclusion of moisture, in a cell of rather large cell constant (electrodes each $1{\cdot}36$ cm^2, 2 mm apart), which called for fairly large applied voltage. It is also of interest that Addenbrooke[1] in discussing Anderson's work, mentioned that he had earlier obtained a specific resistance of 10^{11} *megohms* for bromine. Clearly *ohms* was intended, judging from his data. Although he accepted Anderson's values, his own lies closer to ours (assuming it to be expressed in ohms).

The resistance curves of solid bromine during short recording periods with intermediate short-circuiting were similar in shape to those of the liquid. For longer recording time and intermediate switching of polarity the shapes of the curves were always like that of curve I in Fig. 3, showing that the effect of previous polarisation was negligible.

II—THERMAL CONDUCTIVITY

No previous data on the thermal conductivity of liquid bromine were located. It was decided to employ a hot wire method, the principle of which has been adequately discussed by Hutchinson.[9] Thanks are expressed to W. E. Hatton for assistance in applying this method.

EXPERIMENTAL

Apparatus

The cell was made up of a Pyrex tube, 2·79 mm o.d. and 1·57 mm i.d., housing a coil 5·5 cm in length and 0·092 mm in diameter made from tungsten wire 0·012 mm in diameter. Separate leads for current and potential measurement were connected at each end of the tungsten coil. The resistance of the coil in air was 146·809 Ω at 20°.

In the electrical circuit the following elements were connected in series, in a closed loop: a bank of Edison cells with a total e.m.f. of 8 V, decade resistors ranging from 100 to 10,000 Ω to adjust the current level, a calibrated 100-Ω precision resistor with negligible temperature coefficient and the conductivity cell. A precision Rubicon potentiometer with a sensitive galvanometer was used to determine the potential across the cell to within 0·01 mV.

For temperature control a 4-litre beaker with a stirrer was placed in an ordinary constant temperature bath with an insulating cover. The temperature of water in the beaker could be kept constant to about 0·002°, as indicated by a Princo thermometer with divisions in 0·01°. For the measurement at 10°, ice-water was circulated through a coil in the outer bath. The conductivity cell was placed inside the beaker.

Reagents

Reagent-grade toluene and carbon tetrachloride were doubly distilled. By gas chromatography the toluene showed impurities totalling 0·46 area per cent. These consisted of two major impurities, probably paraffin hydrocarbons boiling near toluene, and three traces one of which was most likely benzene. This product should be similar to the analytical-reagent grade used by Challoner and Powell.[8]

Procedure

The cell was dried by evacuation and was loaded in the same manner as the electrical cell, to avoid contact of bromine with the air. At each bath temperature a constant current was applied to the tungsten coil for 1 hr or longer. Potentials through the standard resistor and through the cell were measured at the end of the period. From these values the resistance of the tungsten coil at a definite power level could be calculated. The current was then changed and the determinations repeated. A plot of resistance against power resulted in a straight line, which also served as a check for internal consistency. With a series of bath temperatures, a series of such straight plots was obtained.

For each plot the extrapolated value of resistance at zero power level was the resistance of the coil at the bath temperature. When this resistance was plotted against the bath temperatures, the slope of the resulting straight line plot was equal to the temperature coefficient, α, of the coil.

Choosing a suitable value of power w from a resistance-power plot, its corresponding Δt_1 was obtained by reading ΔR from the plot and multiplying it by α. Δt_1 denoted the temperature difference between the wire and the bath. When a correction term Δt_2, representing the temperature drop across the Pyrex wall, was subtracted from Δt_1, the difference was Δt, the temperature drop across the thin shell of the sample liquid. The value of Δt_2 could be calculated from the dimensions of the cell by means of known formulae.[17]

The values of w and Δt are related by the equation:

$$w = kC\Delta t \tag{1}$$

where k is the thermal conductivity of the sample and C is the cell constant. The latter was determined by calibration experiments with toluene and carbon tetrachloride. For this purpose the data of Challoner and Powell[8] were used because of their apparently high precision (see below) and suitable spacing of temperatures.

RESULTS

Calibration data are listed in Table III and the averaged results obtained with pure bromine are shown in Table IV. The determinations on bromine presented no difficulty in the range from 20 to 50°, with results reproducible to 1 or 2%. Over-all accuracy is estimated at ±5%. The measurement at 10° showed larger scattering and its accuracy is estimated at ±10%. The data are plotted in Fig. 4.

TABLE III.—CALIBRATION OF THERMAL CONDUCTIVITY CELL

Standard	Temp., °*C*	Thermal conductivity[a]	Power (W), *watt*	Δt, °*C*	Cell constant, *cm*
Toluene	10	$3{\cdot}36 \times 10^{-4}$	3×10^{-3}	0·1802	49·5
Toluene	20	$3{\cdot}29 \times 10^{-4}$	3×10^{-3}	0·1935	47·1
Toluene	40	$3{\cdot}15 \times 10^{-4}$	3×10^{-3}	0·1922	49·5
Toluene	50	$3{\cdot}06 \times 10^{-4}$	3×10^{-3}	0·1961	50·0
					Average 49·0
Carbon tetrachloride	10	$2{\cdot}58 \times 10^{-4}$	3×10^{-3}	0·2443	47·6
Carbon tetrachloride	20	$2{\cdot}55 \times 10^{-4}$	3×10^{-3}	0·2372	49·6
Carbon tetrachloride	40	$2{\cdot}48 \times 10^{-4}$	3×10^{-3}	0·2498	48·4
					Average 48·5

[a] Data of Challoner and Powell[3] expressed in cal.cm^{-1}.sec^{-1}.deg^{-1}.

TABLE IV.—THERMAL CONDUCTIVITY OF LIQUID BROMINE
(cell constant 49·0 cm; power 3×10^{-3} W)

Temp., °*C*	Δt, °*C*	Thermal conductivity, *cal.cm^{-1}.sec^{-1}.deg^{-1}*
10	0·2015	$3{\cdot}04 \times 10^{-4}$
20	0·2051	$2{\cdot}98 \times 10^{-4}$
25	0·2087	$2{\cdot}93 \times 10^{-4}$
30	0·2106	$2{\cdot}91 \times 10^{-4}$
40	0·2216	$2{\cdot}76 \times 10^{-4}$
45	0·2303	$2{\cdot}66 \times 10^{-4}$
50	0·2428	$2{\cdot}52 \times 10^{-4}$

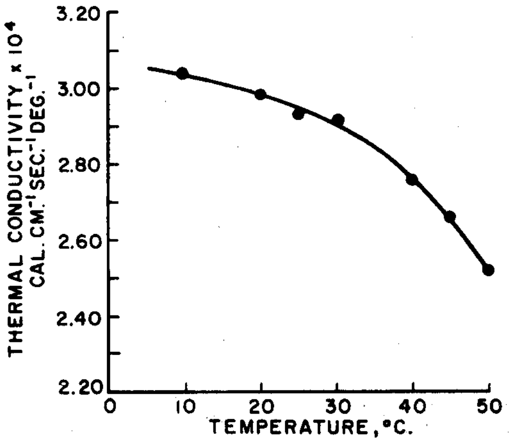

FIG. 4.—Thermal conductivity of bromine.

DISCUSSION

For work with bromine, it is a particular advantage of the hot wire method that the cell can be constructed of materials resistant to corrosion. However, the accuracy of the method is dependent upon calibration against a substance of known thermal conductivity. The thermal conductivity of toluene has been studied by many investigators, whose results have recently been examined statistically by Ziebland.[20] According to his conclusions, the values of Challoner and Powell are about 1·8% too high. If this is the case, our data for bromine are also too high. We have chosen to retain the higher values, particularly because a change would give poorer agreement for the cell constant as found with carbon tetrachloride.

The thermal conductivity of bromine around room temperature lies between those of toluene and carbon tetrachloride. The temperature coefficient is negative, as is also observed with many non-polar liquids, but it is not constant. The drop in thermal conductivity above 30° shown in Fig. 4 is not likely a result of experimental error. While the explanation is uncertain, it must be remembered that bromine is a liquid whose heat capacity, heat of vaporisation and boiling point are all quite low.

Over the range from 0 to 50°, the thermal conductivity of liquid bromine may be approximated by the expression $k = 3{\cdot}04 - 0{\cdot}004\,(t - 10) - 2{\cdot}0 \times 10^{-4}(t - 10)^2$.

III—SURFACE TENSION

A brief literature search failed to reveal any recent determinations of the surface tension of bromine. International Critical Tables[10] lists values which appear to have come almost entirely from unpublished work of W. D. Harkins and G. L. Clark, because the results in cited earlier references are either discordant or difficult to interpret. Mellor[11] gives an equation, based upon data by Ramsay and Aston,[15] which yields surface tension figures about 6% lower than those in International Critical Tables. In no case is there an indication that the bromine used was carefully purified. Both capillary rise and drop weight methods had been employed for the earlier measurements; the former was chosen for use in the present study.

EXPERIMENTAL

Apparatus

A cell was made from two sections of Pyrex tubing 9 inches long, the inside diameters being 2 inches in one case and 1·2 inches in the other. Two precision capillaries were positioned inside the narrower tube, affixed by glass rods to the tube walls. The larger tubes were connected side-by-side through very short sections of 3/8-inch glass tubing at each end, and the ends were sealed and flattened so that the cell would stand upright. An arm at the top of the smaller tube made a connection with the bromine purification train. The cell was placed in a constant temperature bath controllable within 0·01°.

Readings of the bromine levels were made with a Gaertner cathetometer, the vernier of which could be read to within 0·005 cm.

Reagents

Doubly-distilled reagent-grade benzene was used for calibration of the capillaries. Deionised water distilled from alkaline permanganate was employed for the same purpose.

Procedure

The cell was cleaned with a hot mixture of nitric and perchloric acids, rinsed with the above distilled water and thoroughly dried before calibration or connection with the bromine train. After filling and temperature adjustment, readings were taken of the liquid levels in both capillaries and in the wider arm of the cell. The cell was illuminated strongly from behind and no difficulty was encountered in reading the bottom of the bromine meniscus in the capillaries. In the wider tube, the meniscus was read at the lowest point through which transmitted light could be recognised. This was about 0·06 cm below the upper point of contact of liquid bromine with the cell wall.

Although readings were made on both capillaries, only those from one capillary were used in calculating the results. These were from the one which showed closest agreement between calibrations against benzene and water. The other capillary served as a check against any abnormality, such as the presence of a bubble.

Density values used were extrapolated and rounded off from a set obtained on the purified bromine of Hildenbrand *et al.* by O. L. Daniels of this laboratory. His data covered the range 15–30°, falling on a straight line. The gravitational constant was calculated as 980·5 by Helmert's equation. Surface tension data of Richards and Coombs[16] were used in calibrating the capillaries.

RESULTS

The radius of the capillary used for the calculations was taken as 0·005158 cm, this being the mean of the values from calibration against benzene and water. The value from benzene was only 0·1 % larger than that from water.

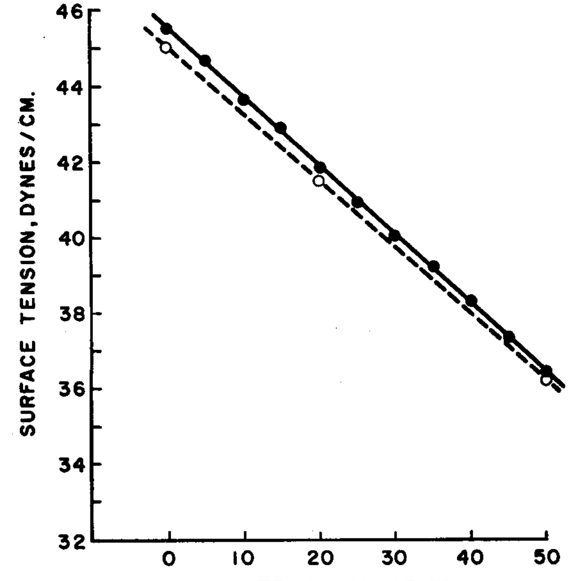

FIG. 5.—Surface tension of bromine: ●—present values, ○—I.C.T. data.

TABLE V—SURFACE TENSION OF LIQUID BROMINE

Temp., °*C*	Capillary rise, *cm*	Density, $g.ml^{-1}$	Surface tension, $dyne.cm^{-1}$
0	5·640	3·191	45·5
5	5·570	3·174	44·7
10	5·470	3·156	43·6
15	5·400	3·140	42·9
20	5·300	3·122	41·8
25	5·210	3·106	40·9
30	5·120	3·088	40·0
35	5·055	3·070	39·2
40	4·960	3·053	38·3
45	4·860	3·036	37·3
50	4·770	3·019	36·4

The surface tension data obtained with bromine are listed in Table V and plotted in Fig. 5 along with those from the International Critical Tables. The equation representing the upper line is:

$$\gamma = 45{\cdot}5 - 0{\cdot}182t$$

where γ is in dyne.cm^{-1} and t is in °C.

DISCUSSION

The maximum error of the present results, based on possible errors in calibration, observed capillary rise and temperature, should not exceed 1·4% or 0·5 dyne.cm^{-1}. This compares favourably with the $\pm 0{\cdot}7$ dyne.cm^{-1} estimate given in the International Critical Tables, and the two sets of data are not separated by more than 0·5 dyne.cm^{-1}. Actually, however, the consistency of each set suggests that the difference between the curves is a real one independent of small random measurement errors. This would point to the purity of the bromine as a possible major item in the discrepancy. If such is the case, the difference in purity probably amounts to several tenths of 1 per cent. One experiment with high purity commercial bromine (impurity less than 0·05%) at 27·0° yielded a surface tension only 0·1 dyne.cm^{-1} below the upper curve. Naturally this is within our experimental error. Nevertheless, it is apparent that the surface tension of bromine is not highly sensitive to the presence of trace impurities.

Zusammenfassung—Die elektrische Leitfähigkeit von sehr reinem Brom ist niedriger als meist in der früheren Literatur angegeben, und die Oberflächenspannung etwas höher. Im flüssigen Bereich können diese Eigenschaften beschrieben werden durch die Gleichungen $\log k = -11{,}372 + 0{,}0128t$ und $\gamma = 45{,}5 - 0{,}182t$, wo k in Ohm^{-1}. cm^{-1}, γ in dyn/cm und t in °C angegeben sind. Erstmals werden Angaben über die Wärmeleitfähigkeit von flüssigem Brom gemacht.

Résumé—La conductivité électrique du brome très pur est inférieure à celle donnée le plus souvant dans la littérature antérieure, et la tension superficielle est légèrement plus élevée. Dans le domaine liquide, ces propriétés peuvent être exprimées par les équations $\log k = -11{,}372 + 0{,}0128t$ et $\alpha = 45{,}5 - 0{,}182t$, où k est exprimé en ohm^{-1} cm^{-1}, α en dyne cm^{-1} et t en °C. Pour la première fois, on fournit des données sur la conductivité thermique du liquide.

REFERENCES

[1] G. L. Addenbrooke, *Proc. Phys. Soc.*, 1928, **40**, 69.
[2] A. I. Anderson, *ibid.*, 1928, **40**, 62.
[3] A. R. Challoner and R. W. Powell, *Proc. Roy. Soc.* 1956, **A238**, 90.
[4] M. Codell and E. Norwitz, *Analyt. Chem.*, 1957, **29**, 967; U.S. Patent 2,929,686, March 22, 1960.
[5] F. Exner, *Ann. Physik u. Chem.*, 1882, **15**, 412.
[6] F. Feigl, *Spot Tests in Inorganic Analysis.* Elsevier Publishing Co., Amsterdam and New York, 5th Ed., 1958, p. 134.
[7] W. Finkelstein, *Z. phys. Chem.*, 1926, **121**, 46.
[8] D. L. Hildenbrand, W. R. Kramer, R. A. MacDonald and D. R. Stull, *J. Amer. Chem. Soc.*, 1958, **80**, 4129.
[9] E. Hutchinson, *Trans. Faraday Soc.*, 1945, **41**, 87.
[10] *International Critical Tables*, Vol. 4. McGraw-Hill and Co., New York, 1928, p. 447.
[11] J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II. Longmans, Green and Co., London, 1922, p. 50.
[12] G. W. Moessen and C. A. Kraus, *Proc. Nat. Acad. Sci. U.S.A.*, 1952, **38**, 1023.
[13] D. G. Prinz, *J. Sci. Instr.*, 1947, **24**, 328.
[14] W. Rabinowitsch, *Z. phys. Chem.*, 1926, **119**, 79.

[15] W. Ramsay and E. Aston, *J. Chem. Soc.*, 1894, **65**, 167.
[16] T. W. Richards and L. B. Coombs, *J. Amer. Chem. Soc.*, 1915, **37**, 1656.
[17] A. F. Schmidt and B. H. Spurlock, Jr., *Trans. Amer. Soc. Mech. Engrs.*, 1954, **76**, 823.
[18] A. G. Sharpe, in Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Suppl. II, Part 1. Longmans, Green and Co., London, 1956, p. 702.
[19] H. Wagner, *Naturwiss.*, 1963, **50**, 224.
[20] H. Ziebland, *Int. J. Heat and Mass Transfer*, 1961, **2**, 273.

Talanta, 1964, Vol. 11, pp. 283 to 293. Pergamon Press Ltd. Printed in Northern Ireland

D_2O EFFECT ON $\Delta H\ddagger$ AND $\Delta S\ddagger$ IN THE IRON^{II}–IRON^{III} ELECTRON-EXCHANGE REACTION

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Summary—The equilibrium constant of the reaction $Fe^{3+} + D_2O \rightarrow FeOD^{2+} + D^+$ has been measured at 0·500 ionic strength at 5°, 15° and 25°. The ΔH and ΔS of this reaction are 9·32 ± 0.56 kcal.mole^{-1} and 17·7 ± 2·0 cal. deg.$^{-1}$ mole^{-1}, respectively. The rates of the electron-exchange reactions $Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+}$ and $Fe^{2+} + {}^*FeOD^{2+} \rightarrow FeOD^{2+} + {}^*Fe^{2+}$ have been measured at 0·500 ionic strength at 5°, 15° and 25°. The enthalpy and entropy of the latter reaction are 11·5 ± 0·5 kcal. mole^{-1} and −4·0 ± 1·8 cal. deg.$^{-1}$ mole^{-1}, respectively.

THE electron exchange-reactions (1) and (2) were studied by Silverman and

$$Fe^{2+} + {}^*Fe^{3+} \xrightarrow{k_0} Fe^{3+} + {}^*Fe^{2+} \tag{1}$$

$$Fe^{2+} + {}^*FeOH^{2+} \xrightarrow{k_H} FeOH^{2+} + {}^*Fe^{2+} \tag{2}$$

Dodson[1] in $H_2O + HClO_4 + NaClO_4$ media with the aid of ^{55}Fe tracer and an end-window Geiger tube to determine the radioactivity of the hydrous iron oxide precipitates obtained at various times throughout the course of the reaction. The energies and entropies of activation reported were 9·9 kcal.mole^{-1} and −25 cal. deg.$^{-1}$ mole^{-1} for reaction (1) and 7·4 kcal.mole^{-1} and −18 cal. deg.$^{-1}$ mole^{-1} for reaction (2).

Reactions (1) and (3) were studied by Hudis and Dodson[2] in

$$Fe^{2+} + {}^*FeOD^{2+} \xrightarrow{k_D} FeOD^{2+} + {}^*Fe^{2+} \tag{3}$$

~90% $D_2O + DClO_4 + NaClO_4$ media using essentially the same techniques. It was found that the rate constants in D_2O media were less than the rate constants of the corresponding reactions in H_2O media. At 7·1° the ratio of the rate constants of reaction (1) in H_2O and D_2O was approximately equal to 2 as was the ratio of the rate constants of reactions (2) and (3). It was not determined whether the substitution of D_2O for H_2O affected the enthalpy or entropy of activation or both. The present-day availability of the isotopic tracer ^{59}Fe and of well-type scintillation counters allows more precise determinations of the rates of these reactions to be made. Hence, it was decided to determine the rates more precisely and to investigate the effect of D_2O on the enthalpies and entropies of activation.

The rate of the iron^{II}-iron^{III} exchange reaction in perchlorate media is given by[1,2]

$$R = \left\{\frac{k_{0,H} + k_H K_H/[H^+]}{1 + K_H/[H^+]}\right\} . [Fe^{II}][Fe^{III}] \tag{4}$$

$$= k_{ob} . [Fe^{II}][Fe^{III}] \tag{5}$$

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in which $k_{0,D}$, k_D, K_D and $[D^+]$ should be substituted for $k_{0,H}$, k_H, K_H and $[H^+]$, respectively, when the exchange occurs in D_2O media, K_H is the equilibrium constant of reaction (6) and K_D the corresponding equilibrium constant in

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \qquad (6)$$

D_2O. Hudis and Dodson[2] reported a determination of K_D at 21·6° and assumed that the enthalpy change for reaction (6) was approximately the same in D_2O as in H_2O but this was insufficient for our purpose. Hence, determinations of K_D at several temperatures are reported here.

EXPERIMENTAL

Reagents

D_2O (>99·8%): Obtained from Nichem Inc., Bethesda, U.S.A., and purified by distillation in an all-glass apparatus. D_2O used in an experiment was reclaimed and purified by vacuum distillation for further use. Anhydrous sodium carbonate and potassium permanganate were used, when necessary, to destroy acids and organic impurities before distillation. The D_2O content of the solvent was determined by measuring the specific gravity at 25°.[3] All D_2O solvent used had a D_2O content greater than 98·5%.

$DClO_4$: Prepared by passing a solution of $NaClO_4$ through a column of deuterated Dowex 50W-X-8 (50–100 mesh) cation-exchange resin. The deuterated form of the cation-exchange resin was obtained as follows. Resin in the sodium form was dehydrated in vacuum at room temperature to eliminate most of the H_2O present, washed with a large amount of D_2O, placed in a 50-ml burette and converted to the deuterated form with a D_2SO_4 solution followed by pure D_2O. D_2SO_4 was prepared beforehand by dissolving anhydrous SO_3 in D_2O. The $DClO_4$ solution obtained from ion exchange was distilled under reduced pressure several times to free it from small amounts of sulphate ion and organic impurities; the final distillate was found to be free from SO_4^{2-}. The concentration of acid in the final solution was determined by titration with a standard NaOH solution.

Crystalline $Fe(ClO_4)_3 \cdot 6H_2O$ *and* $Fe(ClO_4)_2 \cdot 6H_2O$: Obtained from G. F. Smith Chemical Co., U.S.A., and dissolved in dilute $DClO_4$ solutions in D_2O in order to prepare the iron^{III} and iron^{II} perchlorate stock solutions used in the rate experiments; the amount of ordinary water introduced by the crystalline salts was negligible. The methods of standardising the iron concentrations and of preparing the iron^{III} perchlorate solution tagged with ^{59}Fe were entirely similar to those described in a previous paper.[4] Care was taken to oxidise any trace of iron^{II} impurity to iron^{III} in preparing the iron^{III} perchlorate stock solution in D_2O to be used in the spectrophotometric determination of the hydrolysis constant of iron^{III} in D_2O by treating the salt with hot fuming $DClO_4$.[5] The total acid concentration, *i.e.*, the sum $[DClO_4] + 3[Fe^{III}]$, was determined by potentiometric titration with a standard NaOH solution. The concentration of iron^{III} was then determined spectrophotometrically[6] and the $DClO_4$ concentration calculated. It was established by adding known quantities of iron^{III} to known quantities of $HClO_4$ that each mole of iron^{III} added required three equivalents of base in the determination of the total acid concentration.

Anhydrous $NaClO_4$, used to maintain a constant ionic strength, was prepared from $NaCO_3$ and $HClO_4$, recrystallising and drying at 130°.

Measurement of the acid dissociation constant of iron^{III} in D_2O

The methods used to determine the acid dissociation constant of iron^{III} in D_2O were essentially similar to those used by Siddall and Vosburgh.[7] A stock solution containing $5{\cdot}64 \times 10^{-4}M$ iron^{III} and $1{\cdot}29 \times 10^{-2}M$ $DClO_4$ was diluted five-fold in making a set of sample solutions containing a constant concentration of iron^{III} and varying $DClO_4$ concentrations. All solutions were left to stand for a period of 2 weeks before spectrophotometric measurements were made. This was in excess of the necessary length of time.[7] The aging period gives any polynuclear iron^{III} species, which may be present in the more concentrated stock solution, time to dissociate.

Transmittance measurements were made at 340 mμ by means of a Beckman DU spectrophotometer equipped with an insulated cell compartment thermostated on all six sides so as to control the temperature within ±0·1° A set of 10-cm corex cells with carefully measured cell characteristics was used and all absorbance values were corrected to correspond to hypothetical 10·00-cm cells with zero blank corrections.

Measurement of isotope-exchange rate

The main modifications made on the method of Silverman and Dodson[1] for separation of the valence states and for determination of radioactivity in the iron^{II} portion have been described elsewhere.[4] However, further modifications were found to be necessary in the present study to reduce zero-time exchange. At a time *t* approximately 1 ml of reaction mixture was withdrawn and delivered by means of a pipette thermostatted at the temperature of the reaction into an ice-cold quenching solution stirred by a magnetic stirrer. An alcoholic solution of α,α'-dipyridyl was used as quenching solution to increase the solubility of tris-(α,α'-dipyridyl) iron^{II} perchlorate or precipitation of this salt gave incorrect results. Ice-cold Al^{3+}-carrier, ammonium acetate buffer and ammonium nitrate-aqueous ammonia buffer solutions were added successively at controlled intervals. Small fluctuations in the volume of sample withdrawn and in the drainage of the pipette resulted in small fluctuations of the iron^{II} concentration of the samples taken for radioactivity determination. To correct this source of error the absorbance of each radioactive iron^{II} solution at 520 mμ was compared with a standard iron^{II} solution and the radioactivity multiplied by an appropriate factor to take into account the change of iron^{II} concentration.

The reaction mixture was thermostatted to ±0·02° by means of an outer insulated bath controlled to ±1° and an inner bath controlled to ±0·02° by means of opposing heating and cooling devices.

RESULTS

Determination of K_D *in* D_2O

If it is assumed that $[D^+] = [DClO_4] \gg [FeOD^{2+}]$ and that a wavelength can be found where $FeOD^{2+}$ is the main light absorbing species, then equation (7) is readily derived[7] for constant total $[Fe^{III}]$ and varying $[D^+]$.

$$\frac{1}{A} = a + b[D^+] \tag{7}$$

in which A = measured absorbance $\simeq \varepsilon_2 l[FeOD^{2+}]$, $a = 1/\varepsilon_2 l[Fe^{III}]$, $b = 1/K_D \varepsilon_2 l[Fe^{III}]$, ε_2 = molar extinction coefficient of $FeOD^{2+}$ and l = length of absorption cell. When A^{-1} was plotted versus $[D^+]$ an approximate value of K_D was obtained from the relation $K_D = a/b$. With this value of K_D, approximate values of $[Fe^{3+}]$, $[FeOD^{2+}]$, $[D^+] = [DClO_4] + [FeOD^{2+}]$ and the absorbance $\varepsilon_3 l[Fe^{3+}]$ from Fe^{3+} were calculated. Corrected absorbance values for $FeOD^{2+}$ and corrected $[D^+]$ values were now plotted to give new values of *a* and *b* in equation (7). Successive approximations were continued until the value of K_D remained constant; usually one or two cycles yielded constant K_D values. The corrected A and $[D^+]$ values used to obtain K_D are given in Table I and plotted in Fig. 1.

TABLE I.—DETERMINATION OF K_D IN $D_2O + DClO_4 + NaClO_4$ MEDIA

Temp., °*C*	$10^2[D^+]M$	A
25·2 ± 0·1	2·612	0·385
	4·618	0·248
	8·645	0·148
	12·68	0·104
15·0 ± 0·1	2·600	0·251
	4·609	0·154
	8·640	0·0866
	12·67	0·0616
5·0 ± 0·1	2·592	0·1587
	4·604	0·0945
	8·636	0·0518
	12·67	0·0362

$\{[Fe^{III}] = 1{\cdot}128 \times 10^{-4}M;\ \mu = 0{\cdot}500\}$

A weighted least squares[8] calculation of *a* and *b* in equation (7) was made; the results are given in Table II. The relative weight given to each point (x_i, y_i), where $x_i = [D^+]_i$ and $y_i = A_i^{-1}$, was taken to be equal to $(\Delta y_i)^{-2}$. The error, Δy_i, in the value of y_i was considerably larger than the corresponding error in x_i for most data points.

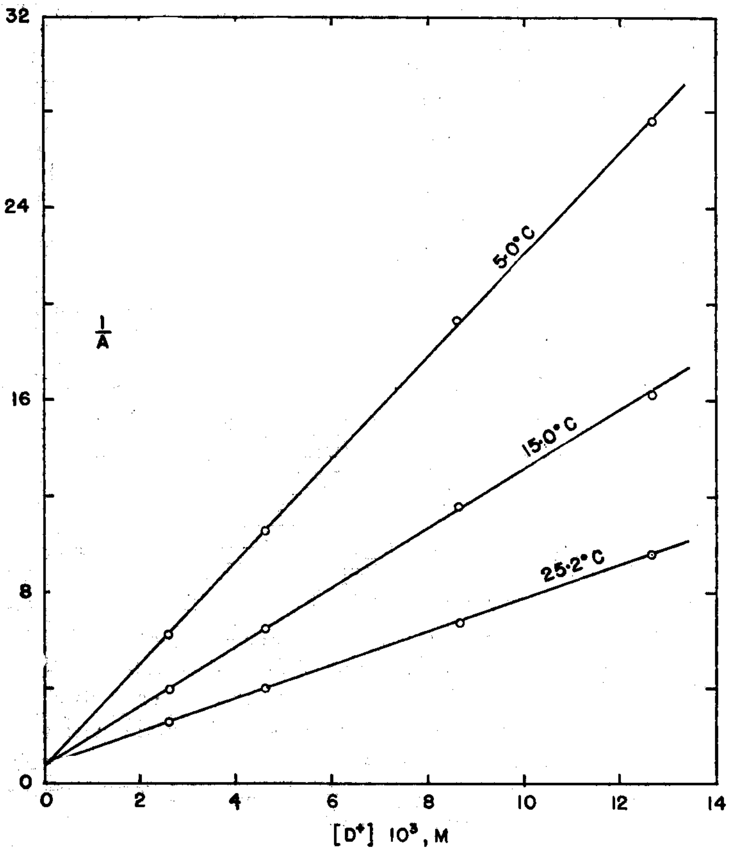

FIG. 1—The inverse of the corrected absorbance for $FeOD^{2+}$ versus the deuterium ion concentration, $[D^+]$.

The error Δy_i was calculated from the relations

$$\Delta y_i = \Delta(A_i^{-1}) = \frac{d}{dT}\left(\frac{1}{A_i}\right)(\Delta T)$$

$$= \frac{1}{2{\cdot}303 A_i^2 T_i}(\Delta T) \qquad (8)$$

in which T_i is the percentage transmittance and ΔT is the error made in reading the percentage transmittance. ΔT was assumed to be constant over the scale used. A plot of $\log K_D$ versus $1/T$, shown in Fig. 4, gave the least squares values of ΔH and ΔS for reaction (6) in D_2O as $9{\cdot}32 \pm 0{\cdot}56$ kcal.mole^{-1} and $17{\cdot}7 \pm 2{\cdot}0$ cal. deg.$^{-1}$ mole^{-1}, respectively.

The values of ϵ_2 at 25°, 15° and 5° were 1130, 1140 and 1150 cm^{-1} M^{-1}, respectively. The corresponding extinction coefficient in H_2O^8 at 25° is 925 cm^{-1} M^{-1}.

TABLE II—WEIGHTED LEAST SQUARES CALCULATION OF a, b AND K_D

Temp., °*C*	a	b	$10^3 K_D M$
25·2	0·787	0·697	1·129 ± 0·048
15·0	0·780	1·236	0·631 ± 0·034
5·0	0·768	2·134	0·360 ± 0·018

Exchange rate in H_2O

Because $\Delta H\ddagger$ and $\Delta S\ddagger$ have to be known rather precisely in order to determine the D_2O effect on each it was necessary to re-determine the rates of reactions (1) and (2) in H_2O. The results are given in Table III. The product $D \cdot k_{ob}$, in which k_{ob} is defined by equations (4) and (5) and $D = 1 + K_H/[H^+]$, the denominator in the expression for k_{ob}, has been plotted versus $1/[H^+]$ in Fig. 2. Excellent precision was obtained. Milburn's semi-empirical expression,[9] equation (9), was used to calculate values of log K_H at $\mu = 0{\cdot}500$ and at each one of the temperatures 18°, 25° and 32°. A regression line, obtained from these values of log K_H, is given in equation (10) and was used to obtain K_H at $\mu = 0{\cdot}500$ and at 5°, 15° and 25°.

TABLE III—RATE OF IRON^{II}–IRON^{III} EXCHANGE IN $H_2O + HClO_4 + NaClO_4$ MEDIA.[a]

Temp., °*C*[b]	$[H^+]M$	$10^4[Fe^{II}]M$	$10^6[Fe^{III}]M$	k_{ob}, *l. mole*$^{-1}$. *sec*$^{-1}$
5·00 ± 0·02	0·500	5·70	3·4	2·16
	0·250	3·17	3·4	3·20
	0·167	2·53	3·4	4·41
	0·125	2·16	14·5	5·51
	0·072	1·27	3·4	8·68
	0·050	1·27	3·4	12·05
15·00 ± 0·02	0·500	1·96	10·0	5·41
	0·250	1·35	10·0	9·19
	0·167	0·903	6·9	12·6
	0·125	0·753	10·4	15·8
	0·072	0·452	6·9	25·6
	0·050	0·301	6·9	36·2
25·00 ± 0·02	0·500	0·758	5·1	14·9
	0·250	0·442	5·1	26·0
	0·167	0·316	5·1	37·3
	0·125	0·253	5·1	47·5

$\mu = 0{\cdot}500$.

[b] The errors given in the temperatures are ranges; the standard deviation probably does not exceed ±0·01°.

$$\log K_H = \log K_H{}^\circ - \frac{4A\sqrt{\mu}}{1 + 2{\cdot}4\sqrt{\mu}} \qquad (9)$$

$$\log K_H = 4{\cdot}531 - 2{\cdot}165 \times 10^3/T \qquad (10)$$

The errors of calculating log K_H by equation (10) were estimated[10] from equation (11), in which Y = log K_H calculated by equation (10), $X = 10^3/T$

$$\sigma(Y) = \sigma\left\{\frac{1}{n} + \frac{(X_i - \bar{X})^2}{\Sigma(X_i - \bar{X})^2}\right\}^{1/2} \qquad (11)$$

$X = \Sigma X_i/n$, n the number of (X_i, Y_i) sets used to obtain equation (10) and σ the standard error of $y_i = \log K_{H_1}$ calculated by equation (9). σ was estimated as the variance of Milburn's experimental values about expression (9).

A least squares treatment of the data shown in Fig. 2, together with the values of K_H calculated from equation (10) and the standard deviations of K_H calculated from equation (11), gave the rate constants and standard deviations listed in Table IV.

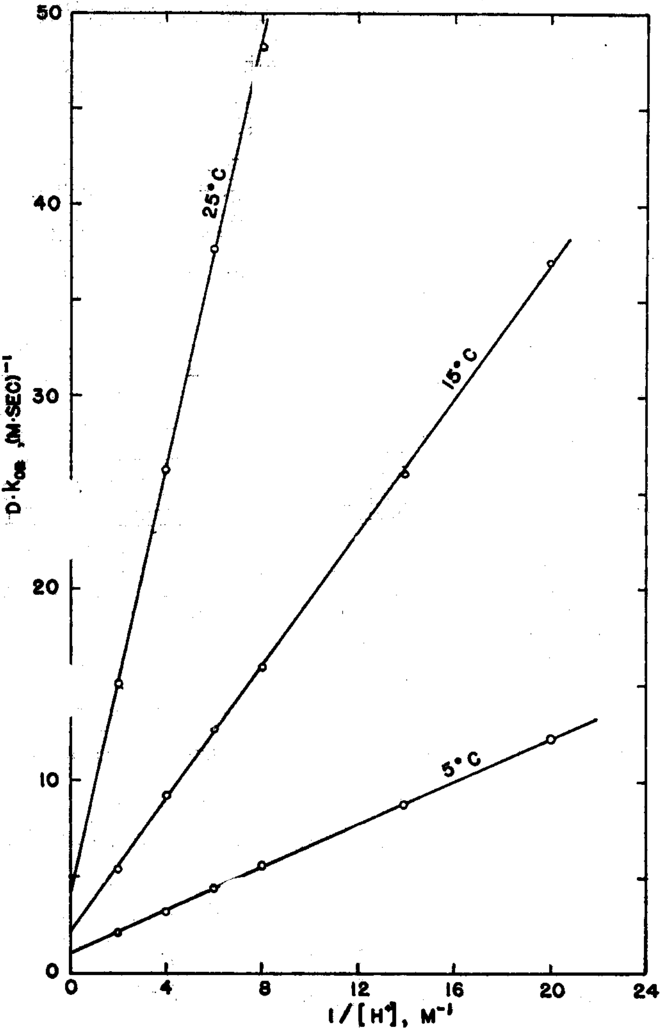

Fig. 2.—Dependence of observed rate constant on acid concentration in H_2O media.

A least squares plot of each log k versus 1/T gave $\Delta H_0^\ddagger = 10{\cdot}5 \pm 0{\cdot}85$ kcal. mole^{-1}, $\Delta S_0^\ddagger = -20{\cdot}6 \pm 3{\cdot}0$ cal. deg^{-1}. mole^{-1} for reaction (1) and $\Delta H_H^\ddagger = 8{\cdot}44 \pm 0{\cdot}47$ kcal.mole^{-1}, $\Delta S_H^\ddagger = -14{\cdot}4 \pm 1{\cdot}6$ cal. deg.$^{-1}$ mole^{-1} for reaction (2). The plot of log k_H versus 1/T is shown in Fig. 4. The values given by Silverman and Dodson[1] for these four quantities are in agreement with the values given here within the error of their measurements. The errors in $\Delta H_0^\ddagger$ and $\Delta S_0^\ddagger$ are still considerable because the steep slope of the D . k_{ob} versus $1/[H^+]$ plots at the higher temperatures gives rise to standard deviations of 8 to 10% in $k_{0,H}$ as may be seen in Table IV.

Exchange rate in D_2O

Exchange rate measurements made at three temperatures are given in Table V. Plots of D . k_{ob} are shown in Fig. 3. The intercepts, $k_{0,D}$, and slopes, $k_D . K_D$, of

TABLE IV.—LEAST SQUARES VALUES OF THE RATE CONSTANTS IN H_2O

Temp., °C	$k_{0,H}$, *l. mole*$^{-1}$. *sec*$^{-1}$	$10^{-3}k_H$, *l. mole*$^{-1}$. *sec*$^{-1}$
5·0	1·04 ± 0·03	0·993 ± 0·043
15·0	2·09 ± 0·16	1·666 ± 0·039
25·0	4·00 ± 0·39	2·978 ± 0·089

$\mu = 0·500$.

TABLE V.—RATE OF IRON^{II}–IRON^{III} EXCHANGE IN $D_2O + DClO_4 + NaClO_4$ MEDIA

Temp., °C	$[D^+]M$	$10^4[Fe^{II}]M$	$10^4[Fe^{III}]M$	k_{ob} l mole^{-1} sec.$^{-1}$
5·00 ± 0·02	0·500	12·63	1·9	0·936
	0·200	7·78	1·9	1·63
	0·125	5·83	1·9	2·36
	0·050	2·67	1·9	5·40
15·00 ± 0·02	0·500	3·72	1·9	2·94
	0·250	2·48	1·9	4·96
	0·167	2·48	1·9	6·95
	0·080	0·992	1·9	13·2
25·00 ± 0·02	0·500	1·83	3·3	8·10
	0·200	0·666	3·3	17·1
	0·150	0·500	3·3	23·6
	0·100	0·333	3·3	34·8

$\mu = 0·500$.

TABLE VI.—LEAST SQUARES VALUES OF THE RATE CONSTANTS IN D_2O

t°C	$k_{0,D}$, *l. mole*$^{-1}$. *sec*$^{-1}$	$k_D K_D$. *sec*$^{-1}$	$10^{-3}k_D$, *l. mole*$^{-1}$. *sec*$^{-1}$
5·0	0·400 ± 0·010	0·249 ± 0·003	0·699 ± 0·032
15·0	1·05 ± 0·06	0·975 ± 0·008	1·528 ± 0·045
25·0	1·0 ± 0·7	3·36 ± 0·10	3·04 ± 0·16

$\mu = 0·500$

the straight lines in Fig. 3 are given in Table VI. The errors reported are least squares standard deviations. The values of k_D were obtained by dividing the slopes by the values of K_D obtained from regression equation (12). The standard deviation of each k_D was obtained from equation (13)

$$4·576 \log K_D = 17·72 - 9·32 . (1/T) . 10^3 \tag{12}$$

$$\left[\frac{\sigma(k_D)}{k_D}\right]^2 = \left[\frac{\sigma(K_D)}{K_D}\right]^2 + \left[\frac{\sigma(k_D K_D)}{k_D K_D}\right]^2 \tag{13}$$

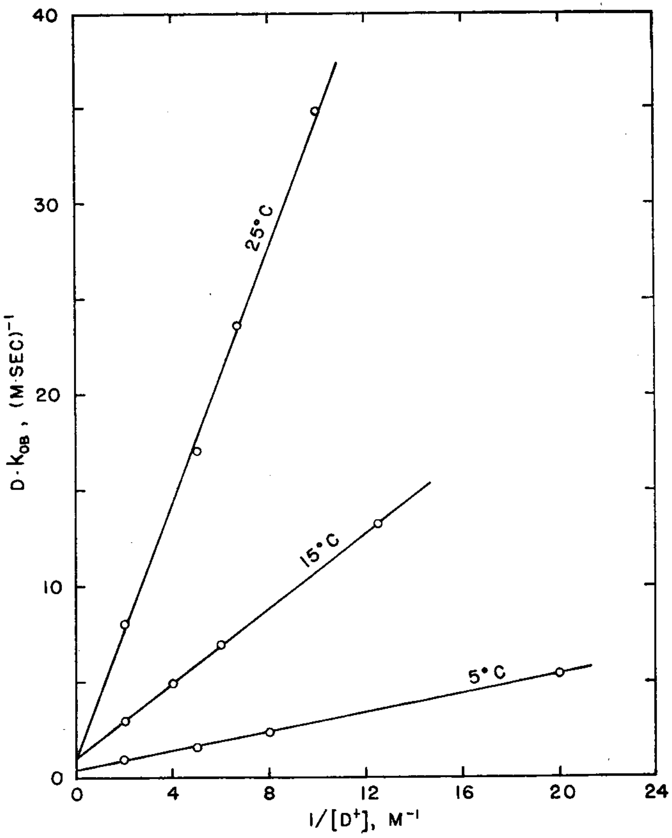

FIG. 3—Dependence of observed rate constant on acid concentration in D_2O media.

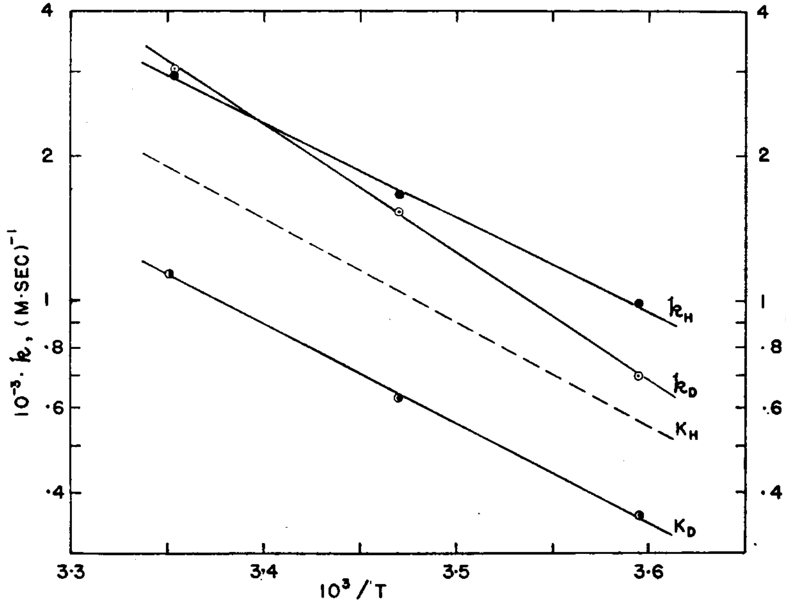

FIG. 4—Equilibrium and rate constants plotted versus ($10^3/T$): ⊙—k_D in D_2O, ●—k_H in H_2O, ◑—k_D in D_2O. The dashed line gives the calculated values of K_H in H_2O.

A least squares plot of log k_D versus $1/T$ shown in Fig. 4 gave the values $\Delta H_D^{\ddagger} = 11{\cdot}5 \pm 0{\cdot}5$ kcal.mole^{-1} and $\Delta S_D^{\ddagger} = -4{\cdot}0 \pm 1{\cdot}8$ cal. deg.$^{-1}$ mole^{-1} for reaction (3). The errors in $k_{0,D}$ do not make a similar plot for this rate constant worthwhile. Qualitatively it can be seen that the D_2O effect on reaction (1) is in agreement with the effect found by Hudis and Dodson.[2]

DISCUSSION

The first acid dissociation constant of $Fe(H_2O)_6^{3+}$ was less in D_2O than in H_2O at the three temperatures and ionic strengths employed in this investigation. Thus at 21·6°, in particular, it was found that K_H/K_D is approximately equal to 1·7 instead of unity as reported by Hudis and Dodson.[2] Despite the fact that $K_H > K_D$, the enthalpy change in H_2O seems to be somewhat larger than in D_2O. However, the difference is small so that it is uncertain.

The differences between $\Delta H_H^{\ddagger}$ and $\Delta H_D^{\ddagger}$ and between $\Delta S_H^{\ddagger}$ and $\Delta S_D^{\ddagger}$ were much larger and seem to be outside of experimental error. The D_2O effect on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is much larger than that predicted by Marcus' equations[11] for an outer-sphere activated complex in which the inner co-ordination shells of the reactant complexes are not shared and in which the inner shell solvent is dielectrically saturated, whereas the solvent outside of the inner shell is dielectrically unsaturated. However, this result was to be expected in view of the small difference between the dielectric constants of H_2O and D_2O and the considerable effect of D_2O on the rate constants as has already been noted.[11] What is more important is the fact that D_2O seems to increase $\Delta H^{\ddagger}$ of the OH^--catalysed reaction more than it increases the $\Delta H^{\ddagger}$ of the Cl^--catalysed reaction[5] given in equation (14). The activation energy of the latter reaction in D_2O[5] was found to

$$Fe^{2+} + {}^*FeCl^{2+} \rightarrow FeCl^{2+} + {}^*Fe^{2+} \qquad (14)$$

be approximately 1·7 kcal. mole^{-1} greater than the activation energy in H_2O. However, the experimental error was sufficiently large so that this difference was not regarded as significant.[5] If the mechanism of the OH^--catalysed reaction is H-atom transfer as compared to either Cl-atom transfer or outer-sphere activated complex mechanisms for reaction (14), then it would be expected that the former reaction would show the larger increase in activation energy in D_2O.

Johnston and Rapp[12] have investigated the tunnelling effect in hydrogen atom transfer reactions of methyl radical with hydrocarbons and concluded that the tunnelling contribution was significant. The end groups in the activated complex $R_1 \cdots H \cdots R_2$ were considered to be so heavy that their contribution to tunnelling was negligible. These authors found that the ratio k_H/k_D increased with decreasing temperature more than the ratio would have increased if the ratio had been dominated only by the difference in the R—H and R—D bond energies in the reactants. Furthermore, a lower limit of 1·5 for the ratio k_H/k_D is given in the high temperature limit. In the present work it was found that the ratio k_H/k_D could be as small as unity. If hydrogen atom transfer, with its accompanying contribution from tunnelling, in the activated complex $[(H_2O)_5Fe^{II}(OH).\ .\ .\ H\ .\ .\ .\ (OH)Fe^{III}(H_2O)_5]^{4+}$ is the most important mechanism for reactions (2) and (3), then it is apparent that isotope effects other than those considered by Johnston and Rapp must be contributing. Furthermore, if the dominant effect on the apparent $\Delta S^{\ddagger}$ in the D-for-H substitution comes from the mass effect on the tunnelling coefficient and if the tunnelling coefficient is assumed to be independent of temperature over the small temperature range used, then it is to be expected that the apparent $\Delta S^\ddagger$ would be larger for H_2O for D_2O. The opposite effect has been observed.

A possible explanation of the $\Delta S^\ddagger$ increase in D_2O is that water molecules are partially or wholly freed from some or all of the hydration shells when the activated complex is formed from the separated reactants. This results in a positive contribution to $\Delta S^\ddagger$ even though the total $\Delta S^\ddagger$ for the activation reaction is negative. Because the entropy of 1 molecule of liquid water is approximately 1·5 cal. deg.$^{-1}$ mole^{-1} greater for $D_2O(l)$ than for $H_2O(l)_7$[13] each 1 mole of water wholly or partially freed in the activation reaction contributes towards a larger $\Delta S^\ddagger$ in D_2O than in H_2O. If an OH^--bridged activated complex is formed, at least one inner shell water molecule must be displaced from the hydrated iron^{II} ion and perhaps other iron-ligand water distances appreciably lengthened in order to accommodate the penetration of $FeOH^{2+}$ with its attached water molecules into the first co-ordination shell of iron^{II} However, the low activation energy of this electron-transfer reaction rather seriously limits the number of inner-shell water molecules which can be wholly or partially displaced. On the other hand, a hydrogen atom transfer does not require any of the inner-ligand water molecules to be wholly displaced.

Qualitatively, the increase of $\Delta H^\ddagger$ in D_2O is readily explained. If one assumes with Bigeleisen[14] that the 3 degrees of vibrational freedom of a water molecule essentially retain their identity in a ligand water molecule, then a hydrated metal ion such as $M(H_2O)_6{}^{+z}$ has 33 vibrational degrees of freedom associated with liberation and with vibration of the water molecules as rigid groups and 18 internal degrees of vibrational freedom inside the 6 ligand water molecules. Each of these liberational and vibrational degrees of freedom has a smaller zero-point energy in $M(D_2O)_6{}^{+z}$ than in $M(H_2O)_6{}^{7+}$. If only a minor fraction[14] of this zero-point energy difference had to be absorbed in forming the activated complex the increase of 3 kcal.mole^{-1} would be readily accounted for.

The D_2O effects reported in this paper, and which seem to be outside of experimental error, point up an obvious danger in measuring the D_2O effect on the rate constant alone without an accompanying investigation of the effect on $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The ratio k_H/k_D at room temperatures is very close to unity and had this ratio been measured at this temperature alone it would have been assumed that a D_2O effect was absent.

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Zusamenfassung—Die Gleichgewichtskonstante der Reaktion $Fe^{3+} + D_2O \rightarrow FeOD^{2+} + D^+$ wurde bei der Ionenstärke 0,500 bei 5°, 15° und 25°C gemessen. Ferner wurden $\Delta H = 9{,}32 \pm 0{,}56$ kcal/mol und $\Delta S = 17{,}7 \pm 2{,}0$ cal/grad.mol gefunden. Die Geschwindigkeiten der Elektronenaustauschreaktionen $Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+}$ und $Fe^{2+} + {}^*FeOD^{2+} \rightarrow {}^*Fe^{2+} + FeOD^{2+}$ wurden bei der Ionenstärke 0,500 bei 5°, 15° und 25°C gemessen. Aktivierungsenthalpie und -entropie der letzten Reaktion wurden zu 11,5 ± 0,5 kcal/mol und −4,0 ± 1,8 cal/grad.mol gefunden.

Résumé—La constante d'équilibre de la réaction $Fe^{3+} + D_2O \rightleftharpoons FeOD^{+2} + D^+$ a été mesurée à force ionique 0,500 et aux températures 5°, 15° et 25°C. Les valeurs ΔH et ΔS de cette réaction sont respectivement 9,32 ± 0,56 kcal . mole^{-1} et 17,7 ± 2,0 cal . deg.$^{-1}$ mole^{-1}. Les vitesses d'échange de l'électron dans les réactions $Fe^{2+} + {}^*Fe^{3+} \rightleftharpoons Fe^{3+} + {}^*Fe^{2+}$ et $Fe^{2+} + {}^*FeOD^{2+} \rightleftharpoons FeOD^{2+} + {}^*Fe^{2+}$ ont été mesurées à force ionique 0,500 et aux températures 5°, 15° et 25°C. L'enthalpie et l'entropie d'activation de cette dernière réaction sont respectivement 11,5 ± 0,5 kcal . mole^{-1} et −4,0 ± 1,8 cal . deg.$^{-1}$ mole^{-1}.

REFERENCES

[1] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, 1952, **56**, 846.
[2] J. Hudis and R. W. Dodson, *J. Amer. Chem. Soc.*, 1956, **78**, 911.
[3] I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water.* McGraw-Hill, New York, 1951, Chap. 1.
[4] W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, 1963, **2**, 176.
[5] N. Sutin, J. K. Rowley and R. W. Dodson, *J. Phys. Chem.*, 1961, **65**, 1248.
[6] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. II. D. Van Nostrand Co., New York, 1949, p. 316.
[7] T. H. Siddall, III, and W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1951, **73**, 4270; R. M. Milburn and W. C. Vosburgh, *ibid.*, 1955, **77**, 1352.
[8] P. G. Guest, *Numerical Methods of Curve Fitting.* Cambridge University Press, 1961, Chap. 6.
[9] R. M. Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.
[10] Owen L. Davies, *Statistical Methods in Research and Production.* Oliver and Boyd, Ltd., London, 3rd ed. (1957).
[11] R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; 1957, **26**, 867.
[12] H. S. Johnston and D. Rapp, *J. Amer. Chem. Soc.*, 1961, **83**, 1.
[13] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties.* Circular of the National Bureau of Standards 500, 1952.
[14] J. Bigeleisen, *J. Chem. Phys.*, 1960, **32**, 1583.

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LEAD-DITHIZONE EQUILIBRIA IN WATER-CARBON TETRACHLORIDE SYSTEMS*

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Summary—Equilibrium of the principal reactions involved in the extraction of lead dithizonate from aqueous solution with carbon tetrachloride (0) have been determined at $\mu = 0{\cdot}1$:

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{2+}][H_2Dz]_0^2} = 5{\cdot}6 \pm 0{\cdot}3 \qquad (5{\cdot}8 \pm 0{\cdot}6 \text{ at } \mu = 0{\cdot}3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{soly. in } CCl_4}{\text{soly. in } H_2O} = \frac{6 \times 10^{-6}}{3 \times 10^{-9}} = 2 \times 10^3$$

$$K_{diss} = \frac{[Pb^{2+}][HDz^-]^2}{[Pb(HDz)_2]} = 7 \times 10^{-16}$$

$$K_{sp} = [Pb^{2+}][HDz^-]^2 = 2 \times 10^{-24} \qquad \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]} = 7 \times 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{2+}][Cit^{3-}]} = 5{\cdot}4 \times 10^5 \qquad \frac{[PbNO_3^+]}{[Pb^{2+}][NO_3^-]} = 0{\cdot}11$$

The pH range for extraction of >99% of lead under analytical conditions (citrate and cyanide present, low equilibrium concentration of dithizone) is 7·5–11·5. Cyanide in the concentrations likely to be used does not significantly decrease the extraction of lead. Above pH 10·85, >99% of the excess dithizone is extracted from the carbon tetrachloride phase into an equal volume of aqueous phase. A pH of 10·8–10·9 is recommended for determination of lead with a carbon tetrachloride solution of dithizone. A variation of *ca.* ~0·2 pH unit from this value causes little error.

DITHIZONE is a valuable reagent both for the separation of lead and its spectrophotometric determination. Although dithizone extraction methods for lead with carbon tetrachloride or chloroform as solvent have now been worked out quite satisfactorily, they rest on an empirical basis. Therefore, it seemed desirable to study a little more closely than heretofore the equilibria existing in the system dithizone-water-carbon tetrachloride, with special reference to the factors bearing on the determination of lead.

EXPERIMENTAL

Reagents

Water. Conductivity water was run through a 20 × 500-mm column of Amberlite IR-120 ion-exchange resin. The content of heavy metals reacting with dithizone at pH 8, as determined spectrophotometrically, at 520 mμ was equivalent to 0·001 ppm of lead. No coloured substances were extracted by carbon tetrachloride. Water thus purified was lower in dithizone-reacting metals than water redistilled in Pyrex apparatus (0·014 ppm of lead).

Hydrochloric acid. A 7*M* solution obtained by isothermal distillation at room temperature (polyethylene beaker) contained heavy metals equivalent to 0·001 ppm of lead.

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* From the Ph.D. thesis of O. B. Mathre, University of Minnesota, 1956.

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Nitric acid. A reagent-quality product contained 0·008 ppm of lead and was used without further purification after boiling out oxides of nitrogen.

Perchloric acid. The 70% acid (reagent grade) available contained only *ca.* 0·001 ppm of lead. Because perchloric acid sometimes contains substances oxidising dithizone, the concentrated acid was diluted with water to $1M$ and shaken for 1 week with a saturated carbon tetrachloride solution of dithizone. The trace of dithizone was removed by extraction with carbon tetrachloride.

Aqueous ammonia. A $9M$ solution obtained by isothermal distillation contained 0·001 ppm of lead. A $12M$ solution prepared by absorbing tank ammonia in water contained 0·0012 ppm of lead.

Sodium hydroxide. Carbonate-free *ca.* $0{\cdot}15M$ sodium hydroxide solution was prepared by passing purified sodium perchlorate solution through a column of Amberlite IRA-410 resin in the hydroxide form and collecting under nitrogen. The heavy metal content of the solution was equivalent to 0·0008 ppm of lead.

Potassium cyanide. A product free from sulphide and containing 0·008 ppm of heavy metals as lead was used without purification. (Some reagent-quality potassium cyanide contained so much sulphide that it could not be used in the dithizone determination of lead.)

Sodium perchlorate. A slight excess of perchloric acid was added to sodium carbonate so as to give a solution *ca.* $0{\cdot}001M$ in acid. This was shaken for 2 days with dithizone in carbon tetrachloride to remove substances oxidising dithizone. The pH was adjusted to 8 and heavy metals were extracted with dithizone. A $6M$ sodium perchlorate solution contained 0·0045 ppm of heavy metals as lead.

Sodium citrate. After dithizone extraction at pH 8, a $0{\cdot}5M$ solution contained 0·003 ppm of lead. *Sodium sulphite* (10%) and *sodium nitrate* ($3M$) solutions purified in like manner contained 0·0015 and 0·002 ppm of metals equivalent to lead.

Lead nitrate. The salt was recrystallised several times from $0{\cdot}01M$ nitric acid and vacuum-dried over potassium hydroxide after grinding to a powder. Determination of lead gravimetrically gave the theoretical value.

Dithizone. Two g of Eastman dithizone were dissolved in 150 ml of reagent-quality chloroform, insoluble material was filtered off, and the filtrate was shaken with four 50-ml portions of dilute purified aqueous ammonia. A small amount of sulphur dioxide was passed into the combined aqueous extracts and an extraction was made with 25 ml of chloroform, which was discarded. Sulphur dioxide was passed into the aqueous solution until acidic and dithizone was extracted with four 30-ml portions of chloroform which had been washed with 1:100 aqueous ammonia just before use. The chloroform solution was filtered through a pledget of glass wool into a flask. An equal volume of carbon tetrachloride was added and nitrogen was bubbled through the solution at 40°. When the volume had been reduced to 50 ml, the liquid was cooled in ice and filtered through sintered glass. The solid dithizone as washed with a little carbon tetrachloride and vacuum-dried over potassium hydroxide for 2 weeks.

The dithizone content of the product was determined by photometric titration with silver. Ten-ml portions of *ca.* $5 \times 10^{-5}M$ dithizone in carbon tetrachloride were shaken with 10-ml portions of $0{\cdot}1N$ sulphuric acid containing varying amounts of silver (less than required for the stoichiometric ratio). A plot of the absorbance of the carbon tetrachloride at 620 mμ against the amount of silver gave a straight line whose intersection with the silver axis indicated the equivalence point. Two batches of dithizone gave the following replicate values (%) for active reagent:

99·9	100·1
99·8	99·8
100·2	99·8
99·8	100·2
100·1	

The molar absorptivities of dithizone in carbon tetrachloride (solutions prepared by weighing out solid dithizone) at 25°, based on an average of 8 absorbance measurements of $0{\cdot}25-1{\cdot}26 \times 10^{-4}M$ solutions (standard deviations *ca.* 1%), were found to be

$$1{\cdot}90 \times 10^4 \text{ at } 450\ \text{m}\mu$$
$$4{\cdot}69 \times 10^4 \text{ at } 510\ \text{m}\mu$$
$$3{\cdot}17 \times 10^4 \text{ at } 620\ \text{m}\mu$$

and $\varepsilon_{620}/\varepsilon_{450} = 1{\cdot}67$. A Beckman DU spectrophotometer was used for these measurements. Weber and Vouk[1] report $\varepsilon_{450} = 2{\cdot}14 \times 10^4$, $\varepsilon_{620} = 3{\cdot}64 \times 10^4$ and $\varepsilon_{630}/\varepsilon_{450} = 1{\cdot}70$.

Lead dithizonate. The solid was prepared in two ways:

(1) A 0·01% solution of dithizone in chloroform was shaken with an ammoniacal cyanide solution containing 95% of the theoretical amount of lead required to react with the dithizone. The filtered chloroform phase was evaporated to small volume at 40° in the dark with a stream of purified

nitrogen. The suspension of lead dithizonate was cooled in ice and the microcrystalline lead dithizonate was collected on a sintered-glass filter. The product was vacuum dried over potassium hydroxide.

(2) Lead nitrate in 0·001M perchloric acid was added slowly to an aqueous ammonia-potassium cyanide-ammonium sulphide mixture of pH 10·5 which was $10^{-4}M$ in dithizone. The precipitated lead dithizonate was filtered off, washed with dilute aqueous ammonia, water, alcohol and chloroform, then vacuum-dried over potassium hydroxide.

Lead was determined in the products by precipitation as the chromate after destroying dithizone with perchloric acid. Dithizonate radical was determined spectrophotometrically after reverting a weighed amount of the solid by shaking the carbon tetrachloride solution with 0·1M hydrochloric acid. As a check on the gravimetric lead determination, a portion of the acid was analysed for lead spectrophotometrically with dithizone. The analytical figures shown in Table I were obtained.

TABLE I

	Pb, %	Dithizonate radical, %	Pb + dithizonate, %	% Dithizonate: % Pb
Preparation (1)	28·9 (grav.) 28·9 (grav.) 28·7	70·7	99·5	2·444
Preparation (2)	28·5 (grav.) 28·3 28·6	69·9 70·2	98·55	2·458
Theoretical	28·87	71·13	100·0	2·464

The solid lead dithizonate seems to be approximately 99% pure. If the remainder is water (which is not certain), its amount is not large enough to correspond to a hydrate.

The molar absorptivity of lead dithizonate in carbon tetrachloride at 520 mμ, the wavelength of maximum absorption, was determined by three methods, each average being based on 20 absorbance measurements (Table II). The standard deviation is a little less than 1%. The concentration of lead dithizonate ranged from 5×10^{-6} to $1{\cdot}6 \times 10^{-5}M$; ε was independent of the concentration.

TABLE II.—MOLAR ABSORPTIVITY OF LEAD DITHIZONATE IN CARBON TETRACHLORIDE AT 520 mμ

Method	ε_{520}
(1) Known amounts of lead extracted with 0·005% dithizone from aqueous ammonia-cyanide-sulphite buffer of pH 10·8 into CCl_4.	66,200 ± 500
(2) Solid lead dithizonate [Preparation (1)] dissolved in CCl_4 and absorbance measured. Lead dithizonate dissociated by shaking with dilute HCl and lead determined spectrophotometrically by mono colour dithizone method. These values were checked by determination of dithizone in original CCl_4 solution.	66,300 ± 600
(3) Absorbance of CCl_4 solutions of solid lead dithizonate measured and lead determined by spectrophotometric titration with standard $AgNO_3$ solution.	66,600 ± 500

The molar absorptivity-wavelength curve of lead dithizonate in carbon tetrachloride is reproduced in Fig. 1. Weber and Vouk[1] report $\varepsilon_{520} = 7{\cdot}29 \times 10^4$ and $\varepsilon_{620} = 3{\cdot}9 \times 10^3$ for lead dithizonate in carbon tetrachloride.

Carbon tetrachloride. The reagent-grade product was treated with a few drops of bromine, allowed to stand 2 weeks, shaken with 10% sodium hydroxide, refluxed for 4 hr with the same solution, washed free from alkali, refluxed with 10% aqueous hydroxylamine hydrochloride solution for 0·5 hr, washed with water, dried with Drierite and finally distilled from calcium oxide. The purified product was stored in a refrigerator.

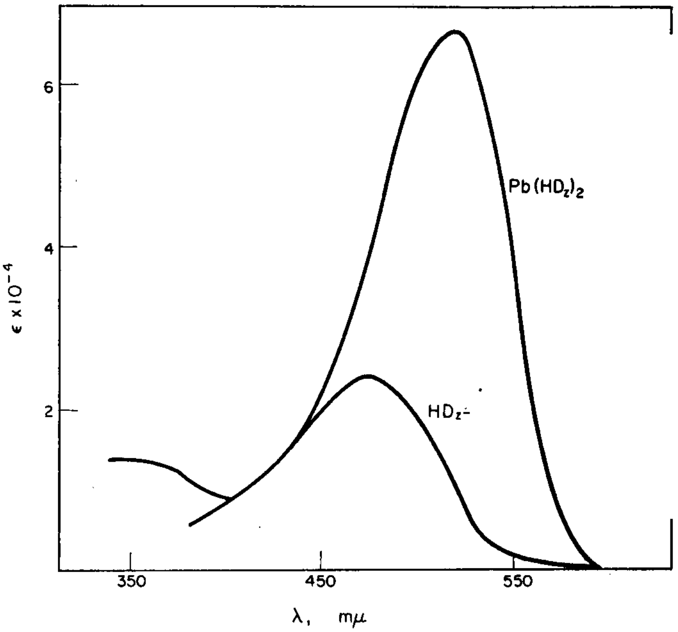

FIG. 1.—Molar absorptivity curves of lead dithizonate, $Pb(HDz)_2$, in carbon tetrachloride, and primary dithizonate ion, HDz^-, in $0{\cdot}01M$ sodium hydroxide.

Dilute dithizone solutions prepared from carbon tetrachloride purified in this way show little decomposition in 1 week. For example, a $1{\cdot}29 \times 10^{-5}M$ dithizone solution kept in the dark at 23 ± 3° decreased in strength by about 1·5% after 1 week, as shown by the decrease in absorbance at 620 mμ (Table III).

TABLE III

Time, *days*	A_{450}	A_{510}	A_{620}
0	0·256	0·066	0·422
1	0·256	0·065	0·419
3	0·258	0·066	0·423
7	0·259	0·067	0·416

Used carbon tetrachloride was reclaimed by shaking with concentrated sulphuric acid, in portions one-tenth the volume of the carbon tetrachloride, until the acid remained colourless; washing with water and 1% sodium hydroxide; drying with Drierite and distilling from calcium oxide. Carbon tetrachloride reclaimed five times was used to prepare a $1{\cdot}99 \times 10^{-5}M$ dithizone solution, which after 10 days at room temperature in the dark gave a decrease of only *ca.* 1% in absorbance at 620 mμ.

Analytical-grade carbon tetrachloride which was not purified gives unstable dithizone solutions. "Analysed" carbon tetrachloride from two U.S. manufacturers gave *ca.* $5 \times 10^{-5}M$ dithizone solutions whose absorbance at 620 mμ decreased 14 and 41%, respectively after 10 days at room temperature in the dark.

EQUILIBRIA IN THE LEAD-DITHIZONE-WATER-CARBON TETRACHLORIDE SYSTEM

The equilibrium constant for the extraction reaction

$$Pb^{2+} + \underset{o}{2H_2Dz} \rightleftharpoons \underset{o}{Pb(HDz)_2} + 2H^+$$

(o = organic, *i.e.*, carbon tetrachloride, phase) is the *extraction constant* (at a specified ionic strength)

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{2+}][H_2Dz]_0^2} \tag{1}$$

If the only lead species in the system are Pb^{2+} and $[Pb(HDz)_2]_0$, the *extraction coefficient*, the ratio of concentrations of lead in the organic and aqueous phases, is given by

$$E = \frac{[Pb(HDz)_2]_0}{[Pb^{2+}]} = K_{ex}\frac{[H_2Dz]_0^2}{(aH^+)^2} \tag{2}$$

In practice, other lead species will be present in the aqueous phase, so that

$$E = \frac{[Pb(HDz)_2]_0}{\Sigma[Pb]} \tag{3}$$

The equilibrium constants involving these species, relating their concentrations to $[Pb^{2+}]$, must then be known before E can be calculated as a function of $[H_2Dz]_0$ and aH^+. The possible presence of the following in the aqueous phase must be considered:

1. Hydroxo-lead species [$PbOH^+$, $Pb(OH)_2$, *etc.*],
2. Dithizone-lead species [$PbHDz^+$, $Pb(HDz)_2$],
3. Lead complexes with anions (cyanide, citrate, *etc.*).

The equilibrium constants for these species will be symbolised and defined as follows:

$$k_1 = \frac{[PbOH^+](aH^+)}{[Pb^{2+}]} \tag{4a}$$

$$k_2 = \frac{[Pb(OH)_2](aH^+)^2}{[Pb^{2+}]} \tag{4b}$$

$$k_3 = \frac{[HPbO_2^-](aH^+)}{[Pb^{2+}]} \tag{4c}$$

$$k_{d1} = \frac{[PbHDz^+]}{[Pb^{2+}][HDz^-]} \tag{4d}$$

$$k_{d2} = \frac{[Pb(HDz)_2]}{[Pb^{2+}][HDz^-]^2} \tag{4e}$$

$$k_{x1} = \frac{[PbX^+]}{[Pb^{2+}][X^-]} \tag{4f}$$

$$k_{x2} = \frac{[PbX_2]}{[Pb^{2+}][X^-]^2}, \textit{ etc.} \tag{4g}$$

X represents a singly (or doubly) charged complexing anion. The values of the constants hold for a specified ionic strength.

The total concentration of lead in the aqueous phase is

$$\Sigma[\mathrm{Pb}] = [\mathrm{Pb}^{2+}] + [\mathrm{PbOH}^+] + \ldots [\mathrm{PbHDz}^-] + \ldots + [\mathrm{PbX}^+] + \ldots$$

$$= [\mathrm{Pb}^{2+}] \times \left(1 + \frac{k_1}{aH^+} + \ldots k_{d1}[\mathrm{HDz}^-] + \ldots k_{x1}[\mathrm{X}^-] + \ldots\right) \qquad (5)$$

and

$$[\mathrm{Pb}^{2+}] = \frac{\Sigma[\mathrm{Pb}]}{\left(1 + \frac{k_1}{aH^+} + \ldots k_{d1}[\mathrm{HDz}^-] + \ldots k_{x1}[\mathrm{X}^-] + \ldots\right)} \qquad (6)$$

Substitution of (6) into (1) and rearrangement give

$$E = \frac{K_{ex}[\mathrm{H_2Dz}]_0^2}{(aH^+)^2\left\{1 + \frac{k_1}{aH^+} + \ldots k_{d1}[\mathrm{HDz}^-] + \ldots k_{x1}[\mathrm{X}^-] + \ldots\right\}} \qquad (7)$$

or

$$E = \frac{K_{ex}[\mathrm{H_2Dz}]_0^2}{(aH^+)^2 + k_1(aH^+) + k_2 + \frac{k_3}{(aH^+)} + k_{d1}(aH^+)^2[\mathrm{HDz}^-] + \ldots k_{x1}(aH^+)^2[\mathrm{X}^-] + \ldots}$$

If O = original concentration of H_2Dz in carbon tetrachloride and phase volumes are equal: $[\mathrm{H_2Dz}]_0 = \frac{7 \times 10^8(aH^+)O}{1 + 7 \times 10^8(aH^+)}$. E should be independent of the lead concentration. It has been assumed that there is no polymerisation of any lead or dithizone species in either phase. Moreover, it has been assumed that no secondary lead dithizonate, PbDz, is formed. There is no experimental evidence to the contrary.

Except when otherwise noted, the constants reported in this paper refer to an ionic strength of 0·1*M* and a temperature of 25 ± 1°. The following values for the hydrolysis constants of lead ion, calculated to $\mu = 0{\cdot}1$, have been used:

$$k_1 = 3 \times 10^{-7}, \qquad k_2 = 3 \times 10^{-18}, \qquad k_3 = 7 \times 10^{-29}.$$

The values of k_1 and k_2 are based on the constants reported by Garrett *et al.*[2] and that of k_3 is derived from the dithizone extractability of lead in alkaline solutions as discussed later. The following activity coefficients have been used for $\mu = 0{\cdot}1$:

$$\gamma_{\mathrm{Pb}^{2+}} = 0{\cdot}37, \qquad \gamma_{\mathrm{PbOH}^+} = 0{\cdot}79, \qquad \gamma_{\mathrm{HPbO_2}^-} = 0{\cdot}80.$$

Solubility of lead dithizonate in carbon tetrachloride

As usually obtained, solid lead dithizonate has such a small particle size that it shows greater than normal solubility in carbon tetrachloride and even after shaking for 1 day its solubility is slightly greater than the true value. The recrystallisation of the small crystals of lead dithizonate proceeds more rapidly in the presence of an aqueous phase. Therefore, most of the solubility determinations were made by shaking solid lead dithizonate with deoxygenated carbon tetrachloride and an acidic or basic aqueous phase. As originally precipitated in most of these experiments, the lead dithizonate consisted of crystals 2–5 μ in length which grew to larger dimensions (crystal length up to 30 μ) on continued shaking. The rate of attainment of solubility

TABLE IV.—SOLUBILITY OF LEAD DITHIZONATE IN CARBON TETRACHLORIDE AT 25°

Expt. No.	Method	Shaking time, *min*	Solubility, $M \times 10^6$
1	10 mg of lead dithizonate [Preparation (2)] shaken with 150 ml of CCl_4.	1380	6·03
2	10 mg of lead dithizonate shaken with 100 ml of CCl_4 and 50 ml of aqueous ammonia-cyanide-sulphite buffer of pH 10·8.	240	5·55
3	Aqueous and solid phases of (2) shaken with 100 ml of fresh CCl_4.	75	5·65
4	50 ml of aqueous-cyanide-sulphite buffer (pH 10·8) containing 0·004 mmole of Pb and 0·009 mmole of H_2Dz shaken with 100 ml of CCl_4.	200	5·80
5	Aqueous and solid phases of (4) shaken with 100 ml of fresh CCl_4.	65	5·65
6	As in (4) except buffer of pH 9·3.	990	5·52
7	Aqueous and solid phases of (6) shaken with 100 ml of fresh CCl_4.	60	5·75
8	50 ml of 0·1*M* acetic acid-acetate buffer (pH 5·7) containing 0·004 mmole of Pb and 0·02 mmole of H_2Dz shaken with 100 ml of CCl_4.	75	5·65
9	Aqueous and solid phases of (8) shaken with 100 ml of fresh CCl_4.	45	5·70
10	50 ml of 0·1*M* acetic acid-acetate buffer (pH 4·3) containing 0·05 mmole of Pb and 0·05 mmole of dithizone shaken with 100 ml of CCl_4.	60	5·90
11	Aqueous and solid phases of (1) shaken with 100 ml of fresh CCl_4.	45	5·70
12	50 ml of 0·1*M* perchloric acid-perchlorate mixture (pH 3·05) containing 0·5 mmole of Pb and 0·05 mmole of dithizone shaken with 100 ml of CCl_4.	30	5·65
13	Aqueous and solid phases of (12) shaken with 100 ml of fresh carbon tetrachloride.	50	5·75
			Avg. 5·7 ± 0·1 (4·1 mg of $Pb(HDz)_2$ or 1·2 mg of Pb per litre)[a]

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[a] The first value, $6 \cdot 03 \times 10^{-6}$, has been omitted.

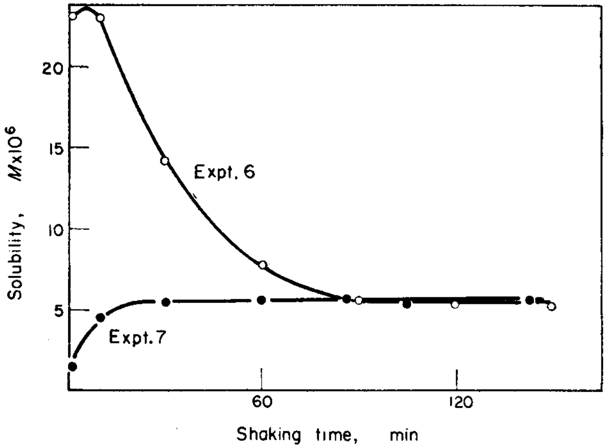

FIG. 2.—Solubility of lead dithizonate in carbon tetrachloride (expts. No. 6 and 7, Table IV) at 25°.

equilibrium from supersaturation increases as the pH decreases. Within experimental error, the same solubilities were obtained by approaching equilibrium from supersaturation and undersaturation (Table IV). Fig. 2 illustrates the rate of attainment of equilibrium. Lead was determined spectrophotometrically as dithizonate at pH 10·8 after suitable dilution of the saturated solution.

Extraction constant of lead dithizonate

K_{ex} can be obtained from distribution determinations with aqueous solutions having a pH less than 4 so that the concentration of $PbOH^+$ can be neglected ($[PbOH^+]/[Pb^{2+}] < 0{\cdot}01$ at $aH^+ = 10^{-4}$). The concentration of $Pb(HDz)_2$ in the aqueous phase can be disregarded under these conditions, and there is no indication that $PbHDz^-$ need be taken into account.

Carbon tetrachloride solutions of dithizone were shaken mechanically for 15 min with perchloric acid-sodium perchlorate solutions of lead at 25 ± 1°. The phases were separated by centrifugation. Dithizone was determined spectrophotometrically in the carbon tetrachloride phase by absorbance measurement at 620 mμ, corrected for $Pb(HDz)_2$. Lead was usually determined in both phases with dithizone at pH 10·8 in the presence of nitrate and cyanide according to the procedure described later. When E was <0·02, lead in the aqueous phase was obtained by difference. The pH of the aqueous phase was determined with a glass electrode (Beckman model G pH meter).

The average of 17 values of K_{ex}, over the pH range 1·5–4·0, is 5·6 ± 0·3 (*ca.* 5% relative standard deviation) (Table V). Least squares treatment of the data gives the same value (Fig. 3). Five determinations of K_{ex} at $\mu = 0{\cdot}3$ yielded an average of 5·8 ± 0·6. The largest source of error in the measurements is probably the pH determination. A deviation of 0·01 in the pH leads to a deviation of about 5% in K_{ex}. Calculations from the lead-dithizone-carbon tetrachloride data of Babko and Pilipenko[3] give a K_{ex} of 8·9; the ionic strength and composition of their buffer solutions are not specified. Koroleff[4] found K_{ex} = 2·4 at pH 4·1–5·6 in acetate-containing solutions.

TABLE V.—EXTRACTION CONSTANT (K_{ex}) OF LEAD DITHIZONATE, WATER-CARBON TETRACHLORIDE ($\mu = 0{\cdot}1$)

pH	$[Pb(HDz)_2]_0 \times 10^5$	$[Pb^{2+}] \times 10^4$	$[H_2Dz]_0 \times 10^5$	K_{ex}
1·50	0·503	9·85	93·6	5·8
1·92[a]	0·805	9·82	46·5	5·5
2·39	0·783	96·7	5·03	5·1
2·42	0·711	96·7	5·03	5·5
2·44	0·974	96·7	4·61	6·2
2·48	1·08	96·7	4·41	6·25
2·77[a]	1·14	30·2	4·54	5·4
2·80	1·67	71·5	3·23	5·6
2·82	0·98	14·0	5·22	5·9
2·89[a]	0·570	9·71	4·22	5·7
3·02	1·13	9·79	4·41	5·4
3·03	1·13	9·79	4·47	5·0
3·08	1·33	9·77	4·00	5·9
3·09	1·32	9·77	4·04	5·5
3·72	0·72	0·364	3·52	5·8
3·92[a]	1·05	1·10	1·58	5·5
3·99	0·401	0·080	3·08	5·5
				Avg. 5·6 ± 0·3

[a] CCl_4 phase initially $5 \times 10^{-6}M$ in lead dithizonate (in addition to dithizone).

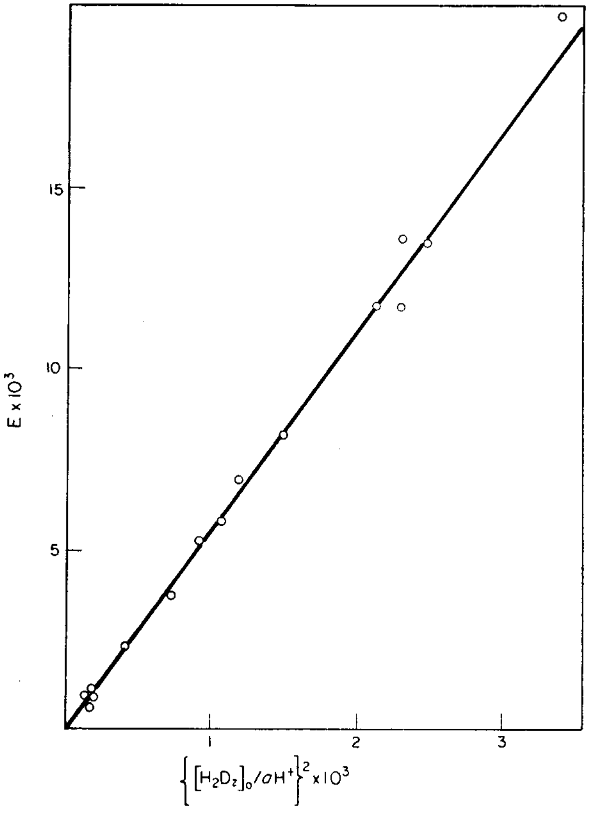

FIG. 3.—Extraction coefficient of lead as a function of $\{[H_2Dz]_0/aH^+\}^2$ ($pK_{ex} = -0{\cdot}75$, $K_{ex} = 5{\cdot}6$).

Partition coefficient and water solubility of lead dithizonate

The partition coefficient $\frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = P$, was determined by obtaining the extraction coefficient of lead at pH 3·68–4·86 with the carbon tetrachloride phase saturated with dithizone and lead dithizonate.

Twenty-five ml portions of carbon tetrachloride saturated with dithizone (solid present) were shaken in a nitrogen atmosphere for 3 hr at 25 ± 1° with 200 ml of sodium perchlorate—perchloric acid solutions containing 0·65 ppm of lead ($\mu = 0{\cdot}1$). Lead was determined spectrophotometrically in both phases ($5{\cdot}7 \pm 0{\cdot}2 \times 10^{-6}M$ in carbon tetrachloride). A 10-cm absorption cell was used in determining the lead in the aqueous phase.

The lead species that must be considered in the aqueous phase are Pb^{2+}, $PbHDz^-$ and $Pb(HDz)_2$. From equation (7):

$$\frac{1}{E} = \frac{(aH^+)^2}{K_{ex}[H_2Gz]_0^2}(1 + k_{d1}[HDz^-]) + \frac{1}{P}$$

$\left(\text{because } k_{d2}(aH^+)^2[HDz^-]^2/K_{ex}[H_2Dz]_0^2 = \frac{1}{P}\right)$. If the term $\frac{(aH^+)^2k_{d1}[HDz^-]}{K_{ex}[H_2Dz]_0^2}$ can be neglected, a plot of $\frac{1}{E}$ against $\frac{(aH^+)^2}{[H_2Dz]_0^2}$ should give a straight line of slope K_{ex}. The data obtained seem to fulfill this condition (Fig. 4). The course of 10 of the 11 points can be represented quite well by a line which has a slope of 5·9 (theoretical 5·6). The intercept of the line is $\frac{1}{P} = 5{\cdot}0 \times 10^{-4}$, or $P = 2 \times 10^{3}$.

The value of k_{d1} has not been determined, but it is not likely to exceed 1×10^{7}. With this value of k_{d1} the slope of the plot of $\frac{1}{E}$ against $\frac{(aH^{+})^{2}}{[H_2Dz]_0^{2}}$ would be 4·85, which

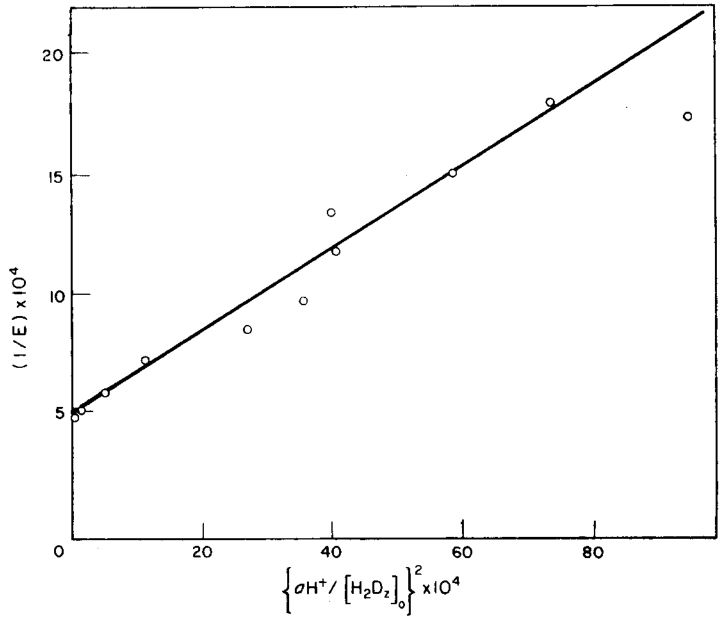

FIG. 4.—Reciprocal of extraction coefficient of lead dithizonate when carbon tetrachloride and aqueous phases are saturated with dithizone and lead dithizonate ($\mu = 0{\cdot}1$, 25°).

differs sufficiently from the slope of the experimental line to make the value implausible. But even if $k_{d1} = 1 \times 10^{7}$, an aqueous solution at pH 4·85 saturated with lead dithizonate and dithizone will be only *ca.* $1 \times 10^{-10}M$ in $PbHDz^{-}$ (and *ca.* $5 \times 10^{-11}M$ in lead ion) compared to *ca.* $3 \times 10^{-9}M$ in lead dithizonate. Thus P would be in error by about 5%, its true value then being $2{\cdot}1 \times 10^{3}$ instead of $2{\cdot}0 \times 10^{3}$ as based on the assumption that all other lead species than $Pb(HDz)_2$ are present in negligible concentrations in this solution. Because of the very low lead concentration in the aqueous phase, the spectrophotometric error in its determination is large, and P may be in error by *ca.* 25%.

From the solubility of lead dithizonate in carbon tetrachloride ($6 \times 10^{-6}M$), the calculated solubility in water (saturated with carbon tetrachloride) is $3 \times 10^{-9}M$.

The dissociation constant of lead dithizonate in water is given by the expression[5]

$$\frac{[Pb^{2+}][HDz^{-}]^{2}}{[Pb(HDz)_2]} = \frac{P_{Pb(HDz)_2}}{K_{ex}}\left(\frac{K_d}{P_d}\right)^{2} = \frac{2 \times 10^{3}}{5{\cdot}6} \times (1{\cdot}4 \times 10^{-9})^{2} = 7 \times 10^{-16}.$$

K_d and P_d are the primary ionisation constant and partition coefficient of dithizone. Because the solubility of lead dithizonate in water (saturated with carbon tetrachloride) is 3×10^{-9}, the solubility product constant of lead dithizonate in water is

$$[Pb^{2+}][HDz^-]^2 = 3 \times 10^{-9} \times 7 \times 10^{-16} = 2 = 10^{-24}.$$

Apparently the only other metal dithizonate whose dissociation constant and solubility product have been determined is primary copper^{II} dithizonate ($K_{diss} = 2 \times 10^{-23}$, $K_{sp} = 2 \times 10^{-31}$).[5] The great difference between the values of K_{ex} for lead and copper (10^{+10}) arises, as would be expected, from the much smaller dissociation constant of copper dithizonate. It may be noted that the solubility product constants of lead and copper dithizonates are much larger than those of the sulphides ($K_{sp\ PbS} = 10^{-27}$, $K_{sp\ CuS} = 10^{-41}$).

Extraction of lead from alkaline solutions

From weakly acidic and weakly basic aqueous solutions the extraction of lead is so complete with even a slight excess of dithizone that the distribution is hardly worth studying. Over a considerable pH range the extraction coefficient of lead is essentially equal to the partition coefficient of molecular lead dithizonate. If a $4 \times 10^{-5}M$ (0·001% w/v) dithizone solution in carbon tetrachloride is shaken with an equal volume of lead solution of such low concentration that the dithizone concentration is not significantly decreased by reaction with lead, the extraction coefficients may be calculated from equation (7), taking P as $2{\cdot}0 \times 10^3$ (Table VI).

TABLE VI

pH	E
6	$1{\cdot}4 \times 10^3$
7	$1{\cdot}9 \times 10^3$
8	$2{\cdot}0 \times 10^3$
9	$2{\cdot}0 \times 10^3$
10	$2{\cdot}0 \times 10^3$
11	$1{\cdot}7 \times 10^3$

From pH 7 to 10, E is essentially the same as P. Above pH 11, the extraction coefficient decreases rapidly because of the formation of biplumbite ion. Determination of the extraction coefficient in an alkaline solution allows the determination of the constant $[HPbO_2^-](aH^+)^3/[Pb^{2+}]$ and a check of equation (7) above pH $\sim$11.

If lead species other than $HPbO_2^-$ can be neglected in the aqueous phase, the extraction coefficient of lead becomes

$$E = \frac{[Pb(HDz)_2]_0}{[HPbO_2^-]} = \frac{K_{ex}[H_2Dz]_0^2(aH^+)}{k_3}$$

$$= \frac{5{\cdot}6 \times (7 \times 10^8)^2[HDz^-]^2(aH^+)^3}{k_3} \quad \text{(because } [H_2Dz]_0 = 7 \times 10^8(aH^+)[HDz^-]\text{)}$$

A plot of log E against log $\{(aH^+)^3[HDz^-]^2\}$ should give a straight line having the intercept log $\dfrac{2\cdot7 \times 10^{18}}{k_3}$

Carbon tetrachloride solutions containing dithizone and lead dithizonate ($1\cdot5 \times 10^{-5}M$) were shaken under nitrogen with sodium hydroxide—sodium perchlorate solutions (from 0·01 to 0·009M sodium hydroxide, $\mu = 0\cdot1$) at 25 ± 1° for 5 min. The phases were separated by centrifugation and the concentration of HDz^- in the aqueous phase was determined by absorbance measurements at 475 mμ ($\varepsilon_{475} = 2\cdot40 \pm 0\cdot02 \times 10^4$). Lead was determined in the carbon tetrachloride phase by shaking with an aqueous ammonia-cyanide-sulphite mixture of pH 10·8 ($[HDz^-] = 10^{-4}M$) and measuring the absorbance at 520 mμ; it was determined similarly in an aliquot of the aqueous phase after acidifying to 0·16M with hydrochloric acid. The pH was determined with an alkaline-range electrode. The values of aH^+ thus obtained agreed within 0·02 with the values calculated from the sodium hydroxide concentration and the activity coefficient $\gamma_{OH} = 0\cdot76$.

From Table VII and Fig. 4, it is seen that the assumption of the presence of $HPbO_2^-$ as the only significant lead species in the pH range 11·9–12·8 is justified.

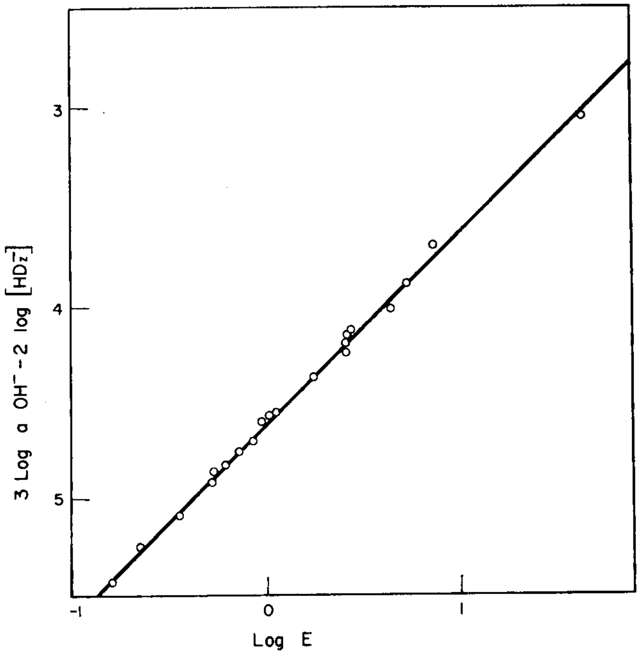

FIG. 5.—Extraction of lead dithizonate from basic solution (E as a function of aOH⁻ and [HDz⁻]).

TABLE VII.—EXTRACTION OF LEAD DITHIZONATE FROM ALKALINE SOLUTION

No. of detns.	pH	E	$K_{ex}\left(\frac{P_d}{K_d}\right)^2 \times \frac{1}{k_3} \times 10^{-46}$
6	11·88	2·68 – 44·5	4·2 ± 0·3
4	12·36	0·37 – 2·75	4·2 ± 0·4
5	12·58	0·29 – 2·9	4·2 ± 0·3
2	12·73	0·56 – 0·75	4·2
4	12·83	0·17 – 0·89	4·3 ± 0·1
Avg.		(0·17 – 44·5)	4·2 ± 0·3

The value of

$$k_3 = \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]}$$

derived from these distribution determinations is 7×10^{-29}. Because the factor 7×10^8 may be in error by *ca.* 7% (1:15), there may be an error of *ca.* 15% in k_3 from this source. The calculated value of $(aHPbO_2^-)(aH^+)^3/(aPb^{2+})$ is $1{\cdot}5 \times 10^{-28}$, which agrees quite well with the value $1{\cdot}1 \times 10^{-28}$ of Garrett and coworkers.[2]

Extraction of lead dithizonate in the presence of cyanide and citrate

From equation (7), using the complex constant

$$\frac{[Pb(CN)_4^{2-}]}{[Pb^{2+}][CN^-]^4} = 2 \times 10^{10} \text{ (Kolthoff and Lingane}^6\text{)*},$$

we calculate the following approximate values for the extraction coefficient of lead for systems in which the original carbon tetrachloride concentration of dithizone is 0·001% ($4 \times 10^{-5}M$) and 0·0001% ($4 \times 10^{-6}M$) and the phases are equal in volume, in the presence of cyanide (0·1*M*) and its absence (Table VIII).

TABLE VIII

pH	E			
	$4 \times 10^{-5}M$ H_2Dz		$4 \times 10^{-6}M$ H_2Dz	
	No CN^-	0·1*M* CN^-	No CN^-	0·1*M* CN^-
10	2×10^3	$1{\cdot}2 \times 10^3$	$1{\cdot}7 \times 10^3$	29
11	$1{\cdot}9 \times 10^3$	$1{\cdot}0 \times 10^3$	$2{\cdot}9 \times 10^2$	20
12	57	56	0·60	0·58

It has been assumed that the amount of lead present is so small that the dithizone concentration is not altered by reaction. Even at the relatively high concentration of 0·1*M*, cyanide should hardly affect the extractability of lead if the original dithizone concentration in the carbon tetrachloride is $4 \times 10^{-5}M$ and the phase volumes are the same or nearly so. However, if the original dithizone concentration is reduced ten-fold to $4 \times 10^{-6}M$ (equivalent to reaction of 90% of the dithizone in a $4 \times 10^{-5}M$ dithizone solution with lead), the effect of cyanide becomes marked.

The negligible effect of *ca.* 0·1*M* cyanide on the extraction of lead at pH 12 was verified experimentally. The distribution of lead between aqueous solutions, which were 0·01*M* in sodium hydroxide and 0·09*M* in potassium cyanide, and carbon tetrachloride-dithizone solutions (10^{-5}–$10^{-4}M$) was determined as described under the extraction of lead from alkaline solutions. The distribution was unaffected by the

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* The value of the constant, derived from the half-wave potential of lead in 1*M* potassium cyanide is approximate and tentative because of the question of the reversibility of the electro-reduction. It seems likely that the constant does not exceed 1×10^{11} (at $\mu = 0{\cdot}1$), for then, contrary to the experimental finding, cyanide would affect the extraction of lead at pH 12.

cyanide. Calculation of

$$\frac{K_{ex} \times (7 \times 10^8)^2}{k_3} \left(= \frac{[Pb(HDz)_2]_0}{[HPbO_2^-][HDz^-]^2(aH^+)^3} \right) \text{ gave the value } 4{\cdot}2 \times 10^{46},$$

the same as the average obtained in the absence of cyanide (Table VII). This agreement also indicates the absence of significant amounts of sulphide in the cyanide used.

The effect of citrate on the extraction of lead dithizonate up to a pH of approximately 8 is in accord with the formation of the complex ion PbCit.$^-$. Kety[7] has already shown that this ion forms in approximately neutral solution (pH 6·95–7·45) and his potentiometric data (corrected for incomplete dissociation of lead nitrate in his reference solution) give the value $1{\cdot}7 \times 10^{-6}$ for the constant $\{[Pb^{2+}][Cit^{3-}]\}/]PbCit^-]$. Below a pH of 7·5 the formation of this complex impedes the extraction of lead dithizonate (*cf.* Figs. 6 and 7) even when the concentration of dithizone is fairly high (0·001%) and the complex constant can thus be easily determined. Forty extraction coefficients determined in the pH range 4 to 6·8 lead to the value $1{\cdot}85 \times 10^{-6}$ for the dissociation constant (or $5{\cdot}4 \times 10^5$ for $[PbCit^-]/\{[Pb^{2+}][Cit^{3-}]\}$) at $\mu = 0{\cdot}1$. The extractability of lead as a function of the citrate concentration was not studied systematically above pH 7·5, but it was observed that under analytical conditions the extraction of lead is as complete in the presence of citrate (0·01*M*) as in its absence (Figs. 6 and 7). There is considerable disagreement concerning the composition of the lead citrate complexes. According to Tikhonov,[10] $Pb(C_6H_5O_7)_2^{4-}$ is formed at pH 6–8 and $PbOH(C_6H_5O_7)^{2-}$ at pH 9–13. The formation of $Pb(C_6H_5O_7)_2^{4-}$ in approximately neutral solutions is not supported by the lead extraction data.

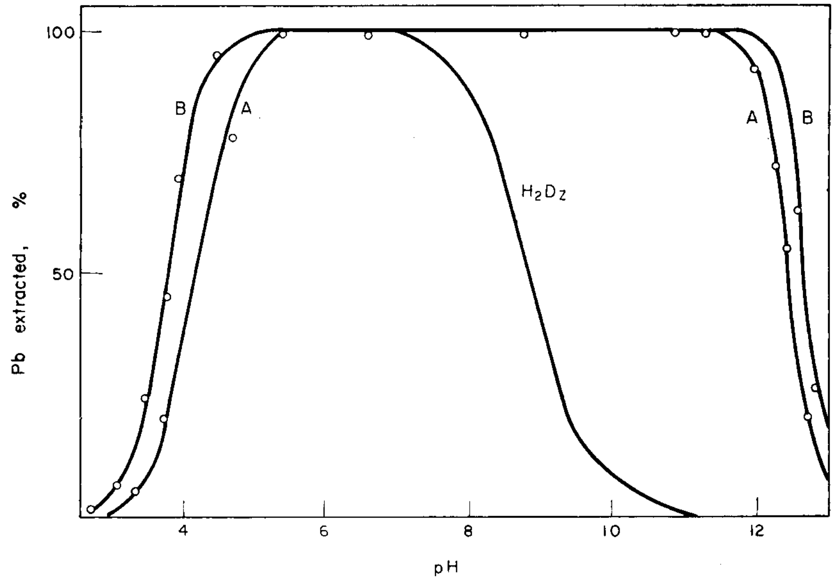

Fig. 6.—Extraction of lead dithizonate and dithizone from sodium perchlorate solution. The solid curves are the calculated curves for the extraction of lead (0·0625 mg in 25 ml aqueous solution, $\mu = 0{\cdot}1$) with 25 ml of 0·001% (w/v) dithizone in carbon tetrachloride (A), and with 25 ml of 0·002% (w/v) dithizone (B). The circles represent experimental values. The extraction curve for dithizone ($_2$Dz) is calculated.

Vouk and Weber[11] studied the extraction of lead dithizonate at pH 5–11 in the presence of citrate and cyanide with more dilute dithizone solutions than used in the present work. Decreasing extraction of lead from *ca.* 0·1*M* citrate solution was noted above a pH of about 8. (These authors obtained low and inconstant values for K_{ex} because they did not take into account the concentration of the lead citrate and cyanide complexes in the aqueous phase when formulating the expression for K_{ex}.)

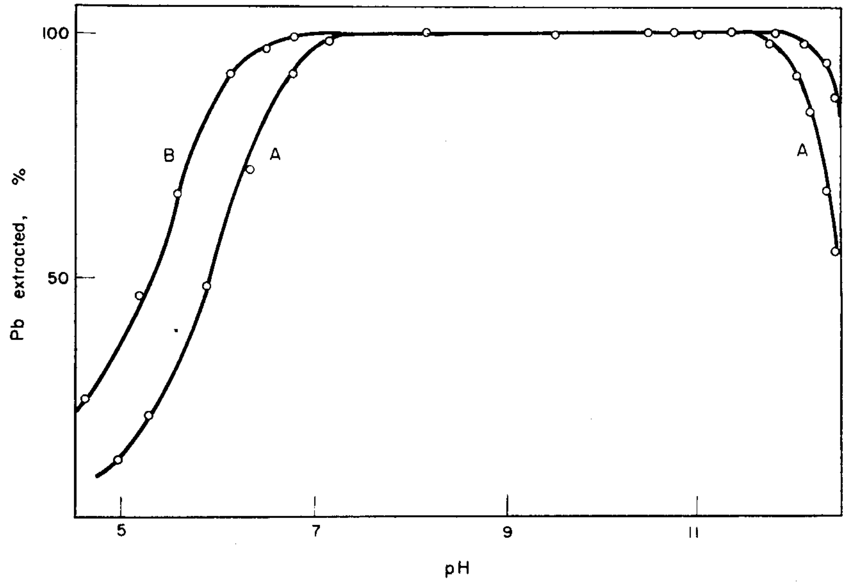

FIG. 7.—Extraction of lead dithizonate from sodium citrate-potassium cyanide solutions. The solid curves are those calculated for the extraction of lead (0·0625 mg in 25 ml of aqueous solution, 0·01*M* in sodium citrate and 0·02*M* in potassium cyanide, $\mu = 0{\cdot}1$) with 25 ml of 0·001% (w/v) dithizone in carbon tetrachloride (A), and with 25 ml of 0·002% (w/v) dithizone (B). The circles represent experimental values.

A few runs were made in the present work to test the effect of nitrate on the lead extraction. From 4 determinations of the extraction coefficient of lead at pH 3·0–3·5, with $[NO_3^-] = 0{\cdot}08$ and $\mu = 0{\cdot}1$, the average value 0·11 was obtained for $[Pb^{2+}] \times [NO_3^-]/[PbNO_3^+]$. Under analytical conditions the effect of nitrate is negligible.

ANALYTICAL CONSIDERATIONS

The spectrophotometric determination of trace amounts of lead usually involves two steps: first, the isolation and separation of lead by dithizone extraction from a basic citrate-cyanide solution, followed by the transfer of the lead to aqueous solution by shaking the carbon tetrachloride (or chloroform) phase with dilute acid; second, the determination proper, in which the aqueous phase is brought to a fixed, appropriate pH and lead is extracted with a standard dithizone solution and the absorbance of the organic phase is measured at a suitable wavelength. The final extraction is also made from a citrate-cyanide medium so that any small amounts of metals escaping separation in the first step will be inactivated. Sometimes sulphite is added to the aqueous solution to provide a reducing environment and lessen the possibility of oxidation of dithizone. Detailed directions for the procedure are available[12] and will not be repeated here. We shall examine the effect of some factors in the procedure on the basis of the equilibria which have been discussed in a general way, beginning with the determination of lead after separation.

Determination of lead

The use of a carbon tetrachloride solution of dithizone allows spectrophotometric determination of lead by a mono colour method at a pH of approximately 11. At and near this pH, lead is virtually completely extracted into the carbon tetrachloride phase with a relatively slight excess of dithizone, whereas the latter is almost completely transferred to the aqueous phase. Other factors being the same, such a method for lead will be preferred to one in which some of the excess dithizone remains in the immiscible organic solvent, because the latter method will require a closer control of the pH and the concentration of the standard dithizone solution.

The theoretical extraction curves of lead—which are also the actual extraction curves—as a function of the pH are shown in Figs. 6 and 7, the former for a perchlorate solution, the latter for a citrate-cyanide solution. With equal volumes of aqueous and carbon tetrachloride phases initially containing, respectively, 2·5 ppm of lead ($1{\cdot}2 \times 10^{-5}M$) and 10 ppm (w/v) dithizone ($4 \times 10^{-5}M$), the calculated pH range for virtually complete (*ca.* 99%) lead extraction from $0{\cdot}01M$ sodium citrate —$0{\cdot}02M$ potassium cyanide is 7·5–11·5. The experimental and calculated values agree very well. The minimum pH for removal of 99% of the excess dithizone from the carbon tetrachloride phase is, from the relation

$$\frac{[\mathrm{HDz}^-]}{[\mathrm{H_2Dz}]_0} = \frac{1{\cdot}4 \times 10^{-9}}{\mathrm{aH}^+},$$

equal to 10·85. The pH range for a mono colour method with carbon tetrachloride as solvent is accordingly approximately 10·8–11·5. In practice one may aim for a pH of 10·8–10·9 to keep safely away from the sharp drop in extractability occurring above pH 11·5. The molar absorptivity of dithizone in carbon tetrachloride is only about 0·07 of that of lead dithizonate at 520 mμ, so that if a few per cent of the excess dithizone remains in the carbon tetrachloride little error results. The error incurred by a 0·2 unit departure from pH 10·8 can almost always be disregarded. Even if the standard curve is established at pH 10·6 and the determination is made at pH 11·0 with 0·001% dithizone, the error would be difficult to detect *ca.* 1% for 5 μg of lead and less for larger amounts of lead.

Because of the limited solubility of lead dithizonate in carbon tetrachloride, the amount of lead in the sample solution should preferably be such that the concentration of lead does not exceed 1·2 μg/ml in the carbon tetrachloride phase. Supersaturated solutions of twice, or even thrice, this concentration are, however, sufficiently stable to allow their use in the spectrophotometric lead determination. Because a carbon tetrachloride solution of lead dithizonate corresponding to 1 μg of lead/ml shows an absorbance of 0·32 at 520 mμ in a 1-cm cell, the concentration limit imposed by solubility does not limit the precision.

The accuracy attainable in the spectrophotometric determination of lead according to the recommended procedure[12] outlined is illustrated in Fig. 8. The accuracy of the reversion method (Irving and Butler[13]) is also represented. The two methods appear to be of comparable accuracy. By the use of a 10-cm cell (25 ml of carbon tetrachloride phase), 1 μg of lead can usually be determined to within 2%. With 5 μg of lead in 10 ml of carbon tetrachloride, the same accuracy is attainable in a 1-cm cell. By reducing the dithizone volume to 5 ml, similar accuracy should be attainable with 2–3 μg of lead.

Carbon tetrachloride is superior to chloroform as a solvent in a mono colour method for lead, because the pH required to transfer 99% of the dithizone from chloroform into an equal volume of aqueous phase is *ca.* 12·5, which is in the range where biplumbite is formed to a considerable extent and *ca.* 10% of the lead is unextracted when a 0·001% dithizone solution is used.

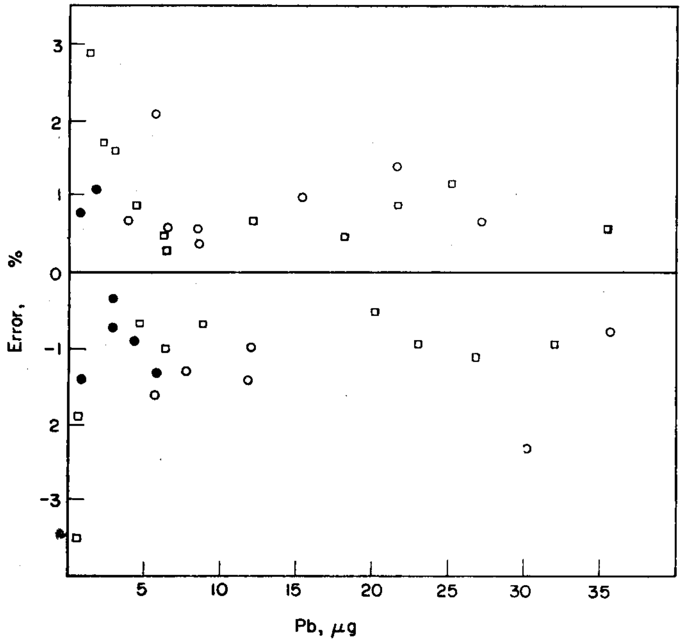

FIG. 8.—Accuracy of determination of lead by mono-colour dithizone method:
○—10 ml of aqueous phase, pH 10·8; 10 ml of 0·001% dithizone in CCl_4; 1-cm cell, 520 mμ;
●—10 ml of aqueous phase, pH 10·8; 25 ml of 0·001% dithizone in CCl_4; 10-cm cell, 520 mμ;
□—Reversion method: 10 of ml aqueous phase, pH 10·8; 25 ml of 0·001% dithizone; reverted with 10 ml of 0·16*M* HNO_3; 1-cm cell (10-cm cell below 8 μg of Pb), 620 mμ.

Separation of lead

The separatory extraction with dithizone in carbon tetrachloride is usually carried out at pH 9–9·5 from an aqueous solution approximately 0·5*M* in citrate and 0·2*M* in cyanide. For a rough calculation of the lead extraction coefficient under these conditions we will use the equilibrium constants valid for an ionic strength of 0·1 and assume that $PbCit^-$ is the principal lead citrate species at pH 9. If the phases are equal in volume and the original concentration of dithizone in the carbon tetrachloride is 0·005% ($2 \times 10^{-4}M$), the extraction coefficient is

$$E = \frac{3{\cdot}8 \times 10^{-8}}{\underset{\mathrm{Pb^{2+}}}{10^{-18}} + \underset{\mathrm{PbOH^{+}}}{3 \times 10^{-16}} + \underset{\mathrm{Pb(OH)_2}}{3 \times 10^{-18}} + \underset{\mathrm{HPbO_2^{-}}}{7 \times 10^{-20}} + \underset{\mathrm{Pb(HDz)_2}}{1{\cdot}9 \times 10^{-11}} + \underset{\mathrm{(PbCit^{-})}}{3 \times 10^{-13}} + \underset{\mathrm{(PbCN)_4^{2-}}}{8 \times 10^{-13}}} = 1{\cdot}9 \times 10^{3}$$

(The amount of lead present is taken to be so small that the concentration of dithizone is not significantly decreased.) The greater part of the lead in the aqueous phase is present as $Pb(HDz)_2$, so that the extraction coefficient is almost the same as the partition coefficient of lead dithizonate. Even when, as in practice, the volume of the carbon tetrachloride phase is 1/5–1/10 that of the aqueous phase, the recovery of lead should be satisfactory. Besides, a second extraction with a fresh portion of dithizone is always made so that there seems to be little likelihood of significant lead loss in the separation step, barring the formation of precipitates, such as calcium phosphate, which can carry down lead. A similar calculation for pH 10 gives $E = 1{\cdot}0 \times 10^{3}$, the lower value being from a smaller fraction of the cyanide being present as HCN at this pH. Because the dithizone extraction constants and the cyanide complex constants of a considerable number of metals are known, the extent of extraction of foreign metals from a cyanide medium can be calculated approximately when required.

The effect of sulphide, which appears to be a not uncommon impurity in alkali cyanides, on the extraction of lead cannot be precisely predicted because of incomplete knowledge of the Pb^{2+}—HS^{-}—S^{2-} system. However, on the assumption that Pb^{2+} is removed only as PbS, it can be demonstrated that very low concentrations of sulphide can have a serious effect on the dithizone extraction of lead. Taking K_{sp} of PbS as 10^{-27}, we obtain the following expression for the concentration of lead dithizonate in the carbon tetrachloride phase at pH 9 when solid lead sulphide is formed:

$$[\mathrm{Pb(HDz)_2}]_0 = \frac{(\Sigma[\mathrm{Pb}] - \Sigma[\mathrm{S}]) \pm \{(\Sigma[\mathrm{Pb}]^{-} - \Sigma[\mathrm{S}])^2 + 4 \times 5{\cdot}6 \times 10^{-5}[\mathrm{H_2Dz}]_0{}^2\}^{1/2}}{2}$$

where $\Sigma[Pb] = [Pb(HDz)_2]_0 + ,q_{PbS}$ the latter term being the quantity of lead sulphide in moles obtained from 1 litre of aqueous lead solution, lead species in the aqueous phase being considered negligible in concentration compared to lead in the carbon tetrachloride phase; and $\Sigma[S] = [HS^-] + q_{PbS}$ (at pH 9, $[S^{=}] = 10^{-4}[HS^-]$). $\Sigma[Pb]$ and $\Sigma[S]$ are thus the initial molar concentrations of lead and sulphide (including HS^-) in the aqueous phase. The two phases are assumed to have the same volume. For example, if the initial dithizone concentration in carbon tetrachloride is $2{\cdot}0 \times 10^{-4}M$, $\Sigma[Pb] = 1{\cdot}0 \times 10^{-6}M$ and $\Sigma[S] = 6 \times 10^{-7}$ (corresponding to 19 μg ΣS per litre), $[Pb(HDz)_2]_0$ at pH 9 is calculated to be $8{\cdot}4 \times 10^{-7}M$ instead of $1{\cdot}0 \times 10^{-6}$ in the absence of sulphide. This illustration is given merely to show the possibility of serious interference by small amounts of sulphide. As long as the concentration of Pb^{2+} in the aqueous phase, in equilibrium with lead dithizonate in the carbon tetrachloride phase, is not great enough to cause the solubility product of lead sulphide to be exceeded, sulphide should have no effect on the extraction, provided other lead-sulphide species do not exist in the aqueous phase. But to assume that this is true would be naive.

Acknowledgment—We are grateful to the Proctor and Gamble Company for providing a summer fellowship for one of us (O.B.M.) in 1955.

Zusammenfassung—Die Gleichgewichtskonstanten der wichtigsten Reaktionen bei der Extraktion von Bleidithizonat aus wäßriger Lösung mit Tetrachlorkohlenstoff (0) wurden bei $\mu = 0,1$ gemessen:

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{2+}][H_2Dz]_0^2} = 5,6 \pm 0,3 \quad (5,8 \pm 0,6 \text{ bei } \mu = 0,3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{Löslichkeit in } CCl_4}{\text{Löslichkeit in } H_2O} = \frac{6 \cdot 10^{-6}}{3 \cdot 10^{-9}} = 2 \cdot 10^3$$

$$K_{diss} = \frac{[Pb^{2+}][HDz^-)^2}{[Pb(HDz)_2]} = 7 \cdot 10^{-16}$$

$$K_{sp} = [Pb^{2+}][HDz^-]^2 = 2 \cdot 10^{-24} \qquad \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]} = 7 \cdot 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{2+}][Cit^{2-}]} = 5,4 \cdot 10^5 \qquad \frac{[PbNO_3^+]}{[Pb^{2+}][NO_3^-]} = 0,11$$

Der p_H-Bereich für Extraktion von über 99% Blei unter analytischen Bedingungen (in Gegenwart von Citrat und Cyanid bei geringer Gleichgewichtskonzentration von Dithizon) ist 7,5–11,5. Cyanid in den üblichen Konzentrationen beeinträchtigt die Extraktion von Blei nicht wesentlich. Über p_H 10,85 werden über 99% des überschüssigen Dithizons von der organischen in das gleiche Volumen wäßriger Phase extrahiert. Ein p_H von 10,8–10,9 wird für die Bestimmung von Blei mit einer Lösung von Dithizon in Tetrachlorkohlenstoff empfohlen. Anderung um etwa 0,2 p_H-Einheiten bringt keinen großen Fehler.

Résumé—Les constantes d'équilibre des réactions principales mises en jeu dans l'extraction du dithizonate de plomb de solutions aqueuses parle tétrachlorure de carbone (0) ont été déterminées à $\mu = 0,1$:

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{++}][H_2Dz_0^2]} = 5,6 \pm 0,3 \quad (5,8 \pm 0,6 \text{ à } \mu = 0,3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{solubilité dans } CCl_4}{\text{solubilité dans } H_2O} = \frac{6 \times 10^{-6}}{3 \times 10^{-9}} = 2 \times 10^8$$

$$K_{diss} = \frac{[Pb^{++}][HDz^-]^2}{[Pb(HDz)_2]} = 7 \times 10^{-16}$$

$$K_{sp} = [Pb^{++}][HDz^-]^2 = 2 \times 10^{-24} \qquad \frac{[HPbO_2^-](aH^+)^3}{[Pb^{++}]} = 7 \times 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{++}][Cit^{=}]} = 5,4 \times 10^5 \qquad \frac{[PbNO_3^+]}{[Pb^{++}][NO_3^-]} = 0,11$$

Le domaine de pH pour l'extraction de 99% du plomb dans des conditions analytiques (citrate et cyanure présents, faible concentration de dithizone à l'équilibre) est 7,5–11,5. Le cyanure aux concentrations où il a été utilisé ne diminue pas d'une manière importante l'extraction du plomb. Au dessus de pH 10,85, 99% de la dithizone en excès est extraite du tétrachlorure de carbone par un égal volume d'eau. Un pH de 10,8–10,9 est recommandé pour la détermination du plomb avec une solution de dithizone dans le tétrachlorure de carbone. Une variation de 0,2 unité de pH de cette valeur ne cause qu'une légère erreur.

REFERENCES

[1] O. A. Weber and V. B. Vouk, *Analyst*, 1960, **85**, 40.
[2] A. Garrett, S. Vallenga and C. Fontana, *J. Amer. Chem. Soc.*, 1939, **61**, 367.
[3] A. K. Babko and A. T. Pilipenko, *Zhur. analit. Khim.*, 1947, **2**, 33.

[4] F. Koroleff, Ph.D. thesis, University of Helsingfors, Helsinki, 1950.
[5] R. W. Geiger and E. B. Sandell, *Analyt. Chim. Acta*, 1953, **8**, 197.
[6] I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience Publishers, New York, 1941, p. 268.
[7] S. Kety, *J. Biol. Chem.*, 1942, **142**, 181.
[8] B. K. Patnaik and S. Pani, *J. Indian Chem. Soc.*, 1957, **34**, 19.
[9] V. E. Panova, *Zhur. neorg. Khim.*, 1957, **2**, 330.
[10] A. S. Tikhonov, *Trudy Voronezh, Gosudarst. Univ.*, 1958, **49**, 79; *Chem. Abs.*, 1961, **55**, 10183.
[11] V. B. Vouk and O. A. Weber, *Analyst*, 1960, **85**, 46.
[12] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York, 3rd ed., 1959, p. 569.
[13] H. Irving and E. Butler, *Analyst*, 1953, **78**, 571.

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THE ANODIC AMPEROMETRIC TITRATION OF LOW CONCENTRATIONS OF NITRITE WITH SULPHAMIC ACID OR CERIUM^{IV} ION*

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Summary—Nitrite at a concentration of approximately $6 \times 10^{-4}M$ in $0{\cdot}05M$ sulphuric acid can be titrated amperometrically at a rotating platinum micro-anode with sulphamic acid or cerium^{IV} ion. Results with sulphamic acid are free from bias and have a standard deviation of about 1%. Titration with cerium^{IV} is less precise, giving results that are high or low according to the method used for end-point location, but is applicable to lower nitrite concentrations than is titration with sulphamic acid.

STOCK and BJORK[1] found that low concentrations of nitrite in acid media can be titrated amperometrically with potassium permanganate solution at a rotating platinum micro-anode. This titrant is not electroactive at potentials from $+1{\cdot}05$ to $+1{\cdot}10$ V with reference to a saturated calomel electrode (S.C.E.), but nitrite under these conditions yields an oxidation limiting current that is proportional to the concentration of nitrite.[2] A titration curve of "L" type is therefore obtained. The present work concerns the application of sulphamic acid and cerium^{IV} ion as alternatives to permanganate in the titration of nitrite by this method.

Hirozawa and Brasted[3] have demonstrated that amperometric titration with sodium nitrite solution at a dropping mercury cathode permits the determination of sulphamic acid in concentrations from 4×10^{-4} to $5 \times 10^{-3}M$. These workers used a hydrochloric acid-potassium chloride supporting solution that contained a low concentration of uranyl ion. In the presence of this ion, nitrite gives a well-defined reduction wave; the limiting current measured at a potential of $-1{\cdot}2$ V *vs.* S.C.E. is proportional to the concentration of nitrite. Sulphamic acid is not reduced under these conditions, so that the titration curve is of "reversed-L" form.

Kolthoff, Harris, and Matsuyama[4] discovered that the simultaneous reduction of uranyl ion catalyses the reduction of nitrate ion at a dropping mercury electrode. Keilin and Otvos[5] found that nitrite in acid solution yields the same reduction wave as nitrate in the presence of uranyl ion. Any appreciable concentration of nitrate that is introduced into the supporting solution used for the amperometric titration of sulphamic acid by Hirozawa and Brasted's method therefore gives a high background current and hence poor end-point discrimination. Hirozawa and Brasted found that the presence of nitrate in the titrant solution gives a positive slope to the pre-equivalence portion of the titration curve and causes low results. The error is tolerable only if the nitrate:nitrite molar ratio does not exceed 2:100. Interference is, of course, caused by phosphate and other substances that precipitate uranyl

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* Taken largely from the thesis submitted by Robert Gesler Bjork in partial fulfilment of the requirements for the M.S. degree.

ion. Because the presence of uranyl ion is not required when changes in the concentration of nitrite are measured in terms of its *oxidation* limiting current, it should be possible to perform nitrite-sulphamic acid titrations at a rotating platinum anode without interference by nitrate or phosphate.

EXPERIMENTAL

Apparatus

Amperometric titration assembly: Titrations were performed in a 100-ml tall-form beaker. This was closed with a cover that carried the nitrogen dispersal tube and the junction tube that accommodated the salt bridge of a large saturated calomel electrode. Holes in the cover were provided for the insertion of the rotating platinum electrode and the jet of the Gilmont 1-ml microburette; these holes were large enough to allow free escape of nitrogen. Except when current readings were taken, the solution in the beaker was stirred at a steady rate of about 200 rpm by means of a small glass-covered magnetic stirrer bar.

Rotated at 600 rpm by a Sargent Synchronous Rotator, the platinum wire micro electrode gave an average current of 14·8 μA in $2 \times 10^{-4}M$ nitrite in deoxygenated 0·05*M* sulphuric acid, when maintained at a potential of +1·05 V *vs.* S.C.E. The actual sensitivity was poorly reproducible and sensitive to electrode pretreatment. However, changes in sensitivity that occurred from run to run did not affect the linearity of the current-to-nitrite concentration relationship within a given run. The electrical equipment was similar to that used previously;[6] a shunt-equipped Cambridge Spot galvanometer of maximum sensitivity 170 mm per μA was used to measure the current.

Reagents

Sodium nitrite solution: Prepare an approximately 0·1*M* solution and standardise against permanganate solution by thiosulphate titration of iodine liberated by the excess of permanganate.[7] This method was used to permit the direct comparison of the results of the present work with those obtained in the amperometric titration of nitrite with permanganate.[1]

Standard (approximately 0·1*M) sulphamic acid solution:* Prepare by the direct weighing of the recrystallised and dried analytical-grade reagent.[8]

Cerium^{IV} *ammonium sulphate solution:* Prepare an approximately 0·1*M* solution in 3% (v/v) sulphuric acid and standardise against arsenious oxide.[8]

Osmium catalyst solution: Prepare approximately 0·01*M* osmium tetroxide in 0·05*M* sulphuric acid.

Anodic voltammetry of sulphamic acid

The current-voltage curve of $1 \times 10^{-3}M$ sulphamic acid in 0·05*M* sulphuric acid at a rotating platinum anode was found to be essentially the same as that of 0·05*M* sulphuric acid alone.

Pretreatment of the platinum electrode

Store the platinum electrode in approximately 10*M* nitric acid. Before use, rotate in deoxygenated 0·1*M* perchloric acid and maintain at zero potential (*i.e.*, short-circuit to the S.C.E.) until the current becomes very small.[9] Rinse well and prepolarise for 10 min at the chosen potential in a solution of composition similar to that to be titrated.

Titration of nitrite with sulphamic acid

Place 50 ml of 0·05*M* sulphuric acid in the titration apparatus and deoxygenate with a stream of nitrogen; this step improves the precision of the titration. Stop the gas stream and introduce the nitrite solution from a microburette until the concentration is about $5 \times 10^{-4}M$. Titrate immediately with small increments of 0·1*M* sulphamic acid at a potential of +1·05 V *vs.* S.C.E. (or at +1·10 V if the nitrite concentration is greater than about $6 \times 10^{-4}M$). Take current readings 15–20 sec after each titrant addition. Temporarily increase the interval to about 40 sec when near the end-point.

Titration of nitrite with cerium^{IV} *ion*

Proceed as described for the titration with sulphamic acid, but add 3 drops of osmium catalyst before titrating with 0·1*M* cerium^{IV} solution.

RESULTS AND DISCUSSION

Titration with sulphamic acid

Well-defined linear L-shaped titration curves were obtained at nitrite concentrations that were not less than $6 \times 10^{-4}M$. The descending arm of the curve became very slightly bowed when the nitrite concentration was lowered to $4 \times 10^{-4}M$. This malformation increased as the initial nitrite concentration was lowered further, and became excessive when the titration of $1 \times 10^{-4}M$ of nitrite was attempted. Results for sets of six replicate titrations of nitrite are given in Table I. In the concentration range 6×10^{-4} to $1 \times 10^{-3}M$ of nitrite, the standard deviations are a little larger than those obtained with permanganate as the titrant.[1] Permanganate, but not sulphamic acid, can be used to titrate nitrite at a concentration as small as $5 \times 10^{-5}M$. These effects are almost certainly caused by differing speeds of reaction; the titration of a given concentration of nitrite can be performed considerably more rapidly with permanganate than with sulphamic acid.

TABLE I.—TITRATION WITH 0·0995*M* SULPHAMIC ACID

Nitrite in 50 ml of 0·05*M* sulphuric acid. Six titrations at each concentration of nitrite.

Nitrite concn., $\times 10^4M$	Potential, *V*	Average error, %	Standard deviation, %
10·00	+1·10	0·0	0·9
8·00	+1·10	0·0	1·0
6·00	+1·05	0·0	0·9
4·00	+1·05	−2·5	2·4

Low results, obtained when permanganate is the titrant and attributed to the instability of nitrite in acid solution,[1] were generally absent in titrations with sulphamic acid. The absence of bias in most of the results given in Table I probably arises from the fortunate compensation of the negative error through loss of nitrous acid by positive errors arising from the non-stoichiometry of the reaction

$$HNO_2 + H_2NSO_3H \rightarrow H_2SO_4 + N_2 + H_2O$$

and the effects of the oxides of nitrogen that are produced in side reactions.[10]

The titration of $1 \times 10^{-3}M$ nitrite in 0·05*M* sulphuric acid-0·1*M* potassium nitrate or 0·05*M* sulphuric acid-0·1*M* phosphoric acid gave results that were within one standard deviation of those given in Table I. There is thus no evidence of interference by massive amounts of nitrate or phosphate ion.

Titration with cerium^{IV} ion

The titrations were all performed at a potential of +1·05 V *vs.* S.C.E. The results exhibited somewhat larger standard deviations than those obtained in the titration of nitrite with permanganate or sulphamic acid. As indicated in Fig. 1, the excess titrant line (which is horizontal in titrations with permanganate or sulphamic acid) has a definite negative slope. An inspection of the current-voltage curves at a rotating platinum electrode of the cerium^{IV}–cerium^{III} couple in sulphuric acid medium[11] suggests this type of behaviour. Positive errors were obtained when the end-point was located by the usual extrapolation of the linear portions of the branches of the titration curve (construction A). An alternative method of location (construction B) shown in Fig. 1 is to produce the descending branch of the titration curve to cut the residual current line (*i.e.*, the horizontal line drawn through the current reading

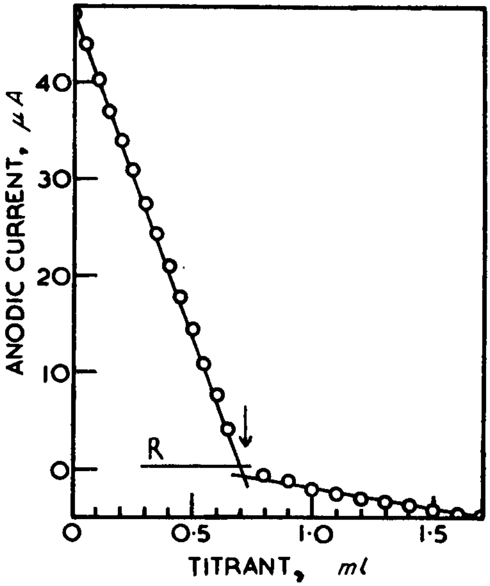

FIG. 1.—Titration of 50 ml of 6·00 × $10^{-4}M$ nitrite with 0·0820M cerium^{IV}
The arrow indicates the stoichiometric end-point.
R is the residual current line.

TABLE II.—TITRATION WITH 0·820M CERIUM^{IV}
Nitrite in 50 ml of 0·05M sulphuric acid. Applied potential, +1·05 V *vs.* S.C.E. Six titrations at each concentration of nitrite.

Nitrite concn., × 10^5M	Construction A		Construction B	
	Average error, %	Standard deviation, %	Average error, %	Standard deviation, %
60·0	+1·4	1·4	−1·9	2·4
40·0	−0·2	0·8	−2·6	3·1
20·0	+2·9	2·6	−2·5	3·0
10·00	+0·8	5·2	−3·3	2·4
8·00	+2·6	2·5	−0·9	1·9
6·00	+5·5	2·4	−0·4	2·7
4·00	+5·7	5·0	−5·2	4·1

obtained in the absence of both nitrite and titrant). The two constructions give results that are comparable in over-all precision and accuracy (Table II). However, neither set of results is free from bias; the over-all average errors for 42 titrations of nitrite in the concentration range 4 × 10^{-5} to 6 × $10^{-4}M$ were +2·7 and −2·4% for constructions A and B, respectively.

From the practical point of view, the negative bias of the results obtained by use of construction B is in line with the known instability of nitrite in acid solution. Readings beyond the end-point are not utilised, so that the determination is expedited. However, the residual current must be frequently checked.

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Zusammenfassung—Nitrit kann in einer Konzentration um $6 \cdot 10^{-4}$ m in 0,05 m Schwefelsäure amperometrisch an einer rotierenden Platinmikroanode mit Amidosulfonsäure oder Cer(IV) titriert werden. Die Ergebnisse mit Amidosulfonsäure sind frei von systematischen Abweichungen und haben eine Standardabweichung von etwa 1%. Die Titration mit Cer(IV) ist weniger genau, gibt je nach der Endpunktsbestimmung zu hohe oder zu niedrige Ergebnisse, aber sie ist bei niedrigeren Nitritkonzentrationen anwendbar als die Titration mit Amidosulfonsäure.

Résumé—On peut titrer ampérométriquement les nitrites, à une concentration d'environ 6×10^{-4} M, en acide sulfurique 0,05 M, avec l'acide sulfamique ou l'ion cérium (IV), au moyen d'une microanode rotative en platine. Les résultats obtenus avec l'acide sulfamique sont exempts de divergences, et présentent un écart type d'environ 1%. Le dosage au cérium (IV) est moins précis, et donne des résultats trop élevés ou trop faibles selon la méthode employée pour déterminer le point final, mais il est applicable à des concentrations en nitrite inférieures à celles qu'autorise le dosage à l'acide sulfamique.

REFERENCES

[1] J. T. Stock and R. G. Bjork, *Microchem. J.*, 1962, **6**, 219.
[2] N. Tanaka and K. Kato, *Bull. Chem. Soc. Japan*, 1956, **29**, 837.
[3] S. T. Hirozawa and R. C. Brasted, *Analyt. Chem.*, 1953, **25**, 221.
[4] I. M. Kolthoff, W. E. Harris and G. Matsuyama, *J. Amer. Chem. Soc.*, 1944, **66**, 1782.
[5] B. Keilin and J. W. Otvos, *ibid.*, 1946, **68**, 2665.
[6] I. M. Kolthoff and J. T. Stock, *Analyst*, 1955, **80**, 860.
[7] I. M. Kolthoff and E. B. Sandell, *Text Book of Quantitative Inorganic Analysis*. Macmillan, New York, 3rd ed., 1953, pp. 573, 592.
[8] I. M. Kolthoff and E. B. Sandell, *op. cit.*, p. 582.
[9] I. M. Kolthoff and N. Tanaka, *Analyt. Chem.*, 1954, **26**, 632.
[10] R. C. Brasted, *ibid.*, 1952, **24**, 1111.
[11] I. M. Kolthoff and E. R. Nightingale, *Analyt. Chim. Acta*, 1957, **17**, 329.

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EFFECTS OF ADSORBED FILMS OF CAMPHOR AND THYMOL ON KINETICS OF THE TITANIUM^{IV}–TITANIUM^{III} ELECTRODE REACTION

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Summary—The effect of contamination of a mercury surface by camphor and thymol on the standard rate constant of the titanium^{IV}–titanium^{III} half reaction in 1*M* tartaric acid has been determined by means of voltage-step and impedance methods. Complications arising from specific adsorption of the electronegative species proved more disturbing to the impedance method than to the voltage-step method. A linear decrease of rate constant with surface coverage is indicated.

It has long been known that adsorption of many surface active substances can affect an electrochemical reaction. The various important features of this problem have already been reviewed by several authors.[1–4] In this work the effect of camphor and thymol, substances of different surface active characteristics, on the Ti^{IV}/Ti^{III} redox reaction has been investigated by measuring the standard rate constants of the reaction in the presence of these surfactants. It was desired to compare the voltage-step method with the impedance method to obtain the rate constant of the reaction.

The electroactive species employed were chosen so that the redox potential of the couple was located as close to the electro-capillary maximum (e.c.m.) potential as possible. No surface-active anion was included in the supporting electrolyte. In such circumstances perturbation of the double layer charge can be neglected. The potential of maximum adsorption can generally be expected to be located close to the e.c.m. potential of the system. However, such a condition has not been fully satisfied by the systems employed. Hence, the electrode coverage was calculated from differential and integral capacity and used for the interpretation of the observations.

EXPERIMENTAL

Apparatus

Cell: The cell was essentially a 100-ml lipless beaker with a rubber stopper which had been bored with a variety of holes to admit a dropping mercury electrode, a stirring rod, a gas disperser, a porous Vycor tube and a glass-frit tube. The cell solution was electrically connected to the S.C.E. through an agar bridge inserted into a glass-frit tube.

Dropping mercury electrode (*d.m.e.*)*:* Because it was essential for the voltage-step method to keep the total resistance of the cell circuit as low as possible, a low resistance d.m.e. was employed. A piece of glass tubing was sealed to 0·04-mm i.d. marine barometer tubing, then drawn out and cut to give a fine tip at one end. Contact was made through a platinum wire sealed into a portion of large bore. The electrical resistance of this type of electrode was in the range of 1·0 to 1·5 Ω.

A sufficiently long life of each mercury drop and small "m" value as well as a fine tipped capillary[5]

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were required to allow the impedance measurements to be carried out satisfactorily. A capillary tube with a pointed tip to meet these requirements was made by stretching under heat an ordinary commercial polarographic capillary and cutting so as to provide a sharp end. The "m" value was $1{\cdot}880 \times 10^{-4}$ g/sec at the mercury head of 70 cm, and the drop life was long enough for the experimental use.

Voltage-step apparatus: The electrical circuit and apparatus were quite similar to those of Laitinen and Roe.[6,7] A voltage divider, a three-way mercury relay switch and an oscilloscopic recording divider were essential parts of the whole assembly.

Impedance Bridge: The assembly used for the a.c. impedance-bridge method consisted of an oscillator, a variable resistance and capacitance, a potentiometer, a mechanical drop-detacher controlled by a timing device, a cathode-ray oscilloscope and a cell containing the solution in question. The entire setup of the assembly, except the cell, has been exhaustively described.[9]

Solutions

All aqueous stock solutions were prepared by dissolving reagent-grade materials, with or without further purification, in distilled water.

H_2SO_4 (1·00*M*) *and* NaOH (2·00*M*)*:* Slightly more concentrated solutions were prepared by dissolving reagent-grade materials in water. These solutions were diluted with water until they gave the required values of concentration in the titration with standard alkali and acid solutions, respectively.

Titanium^{IV} (0·0500*M*)*:* A weighed amount of titanium dioxide was converted into soluble sulphate by fusion with $KHSO_4$, and was dissolved in dilute H_2SO_4. Titanium was precipitated with NaOH, and then redissolved in dilute H_2SO_4. The procedure was repeated, and the final precipitate was dissolved in 1·00*M* H_2SO_4 to make up the required volume.

Tartaric Acid (2*M*)*: d*-Tartaric acid was purified by repeated recrystallisation from water. A weighed amount was dissolved in water.

Camphor (0·1*M*)*: d*-Camphor was dissolved nearly to saturation in methanol and crystallised out by adding an equal volume of water. The procedure was repeated. Camphor thus treated was submitted to further purification by sublimation under reduced pressure.

A weighed amount of purified camphor was dissolved in methanol and then water was added dropwise from a burette until the volume of water added was equal to that of methanol. The solution was made up to volume with a 1:1 mixture of methanol and water.

Thymol (0·1*M*)*:* A weighed amount of thymol, which had been purified by two-fold distillation under reduced pressure, was dissolved in a mixture of methanol and water (1:1), and the solution was left standing overnight until it became clear.

Mercury: Mercury was purified by distillation under reduced pressure.

Ti^{IV}–Ti^{III} *mixed solution:* An equimolar mixture of Ti^{IV} and Ti^{III}, 10 mM in total concentration, was extensively used for the rate determinations. A solution 10 mM in Ti^{IV}, 1*M* in *d*-tartaric acid and 0·2*M* in sodium sulphate was prepared by mixing the stock solutions. A mixture of Ti^{IV} and Ti^{III} was made just before use by electrolysing the Ti^{IV} solution, with constant stirring, at a constant current of about 10 mA between a mercury-pool cathode and a platinum-wire anode inserted into a porous Vycor tube. The solution had been completely deaerated by passing nitrogen, and a thick nitrogen blanket was maintained over the solution during the electrolysis. Under such conditions electrolysis proceeded without an appreciable amount of evolution of hydrogen gas. The concentration ratio of Ti^{IV} to Ti^{III} was determined polarographically. Characteristics of the Ti^{IV} solution were as follows: pH = $1{\cdot}6_5$, $E_{1/2} = -0{\cdot}64$ V *vs.* saturated calomel electrode (S.C.E.), and the diffusion current constant,

$$I = \frac{i_d}{Cm^{2/3}t^{1/6}} = 1{\cdot}34.$$

Blank solution: A solution 1*M* in *d*-tartaric acid and 0·2*M* in sodium sulphate was prepared from stock solutions for the differential capacity measurement. The pH of the solution was $1{\cdot}5_2$.

Special care was taken in introducing thymol and camphor into the cell solution because of their low solubility and high volatility. Injection of a 0·1*M* 50% methanol solution of surfactant with a microlitre syringe pipette was satisfactorily used for this purpose.

Measurement procedure

A. *Voltage-Step Method:* Each time 60 ml of the Ti^{IV}–Ti^{III} solution were used. It was important to keep a thick nitrogen blanket over the solution in the course of the measurement.[5] A voltage step, usually about 5·5 mV, was applied between the mercury pool and the d.m.e. through a three-way mercury relay switch. Because the faradaic current to be determined was quite low, a Tektronix 532 oscilloscope, equipped with an E-type high gain a.c. differential preamplifier, was used for obtaining the current-time relation. The trace photographed on Polaroid-3000 film was reproducible. Sweep rates of 20–50 μsec. cm^{-1} were chosen because the current of interest was expected to be displayed for less than 500 μsec. The faradaic current was obtained by simply subtracting the charging current from the observed current, the former being given by the equation $i_{ch} = V/R_T \times \exp(-t/R_TC_{dl})$, where V, R_T and C_{dl} are the voltage, the total resistance and the double layer capacity, respectively. The total resistance thus obtained was not as reproducible as other quantities, especially in the presence of high concentration of a surfactant, because of the rather large rise time of the preamplifier. Therefore R_T and C_{dl} were determined by means of an a.c. impedance bridge at 1,000 cycles. The resistance was varied from 53 to 56 Ω, corresponding to the change of distance between the electrodes, 2·5 to 5·5 mm. The time between the instant at which the preceding droplet fell from the capillary and the instant at which the voltage step was applied was measured with a 1/100-second electric stop-clock. It was usually 8–10 sec. The area of a drop was calculated assuming its sphericity. There was no perceptible difference in the rate constant between 8 and 10 sec. The equations (2) and (7) of Vielstich and Delahay[11] were used to determine the kinetic parameters of the reaction from the faradaic current at zero time, $i_{t=0}$. Although the maximum of the faradaic current was taken as $i_{t=0}$ instead of estimating an "effective zero time,"[6,7] no appreciable error could be introduced by this procedure, because the slope of the i *vs.* $t^{1/2}$ plot was very small, as expected.

B. *Impedance method: Blank solution:* All the electronic instruments were warmed up for more than 20 min before use. A single frequency of 1,000 cps was employed for the measurement of differential capacity throughout the range of polarisation potential from +0·2 to −1·4 V (*vs.* S.C.E.), while frequencies 200–500 cps. were employed at the certain potentials which corresponded to the equilibrium potential of the titanium couple. Because the detailed description of the operation has been provided by Sherman[9] a brief comment will suffice here.

As differential capacity data are needed after exactly 8·0 sec of the growth of a mercury drop, the timing device was so adjusted that the mechanical drop-detacher was operated at exactly 9·0-sec intervals. At the same time, the horizontal stretch of the image on the oscilloscopic screen was extended to 9·0 divisions. This resulted in a scanning rate of 1·0 division per sec on the screen. When the impedance of the electrode was balanced at 8·0 sec of drop-life, the vertical amplitude of the image on the screen was reduced to a point only at the eighth division line.

Reactants: An identical procedure was employed in determining the impedance of the electrode as was previously described for the blank solution. However, in the presence of the redox couple the dropping mercury cathode was maintained at a constant potential by means of a polarisation unit.[8–10] Only the results obtained at the lower frequencies were analysed because of their better reliability.

RESULTS AND DISCUSSION

Determination of surface coverage

It is first necessary to consider the evaluation of differential double-layer capacity measurements in terms of the surface concentration of adsorbate. If the potential of the redox couple, the electrocapillary maximum, and the potential of maximum adsorption of surfactant were all coincident, the fractional coverage could be calculated from the equation

$$\theta = (C_1 - C)/(C_1 - C_2)$$

where C, C_2 and C_1 are, respectively, the corresponding differential capacities of the partially covered surface, the fully covered surface and the bare surface. From Figs. 1 and 2 the potentials of maximum adsorption of camphor and thymol have been estimated as −0·70 V and −0·55 V, respectively, whereas the redox potential of the Ti couple, at which the coverage has to be estimated, is located at −0·63 V *vs.* S.C.E. It should be better in such circumstances to make use of the integral capacity or the charge density instead of the differential capacity for the calculation of θ. Recently, Breiter and Delahay[12] reported that Frumkin's expression[13] for θ in terms of the charge density gave a good agreement with the thermodynamic surface excess over the entire range of potential including the potential of desorption. Thus, the two kinds of covered fraction were calculated, one from the integral capacity, denoted by θ, and the other from the differential capacity θ'; these are illustrated in Figs. 3a and 3b, and are tabulated in Table I. Integration of the differential capacity was

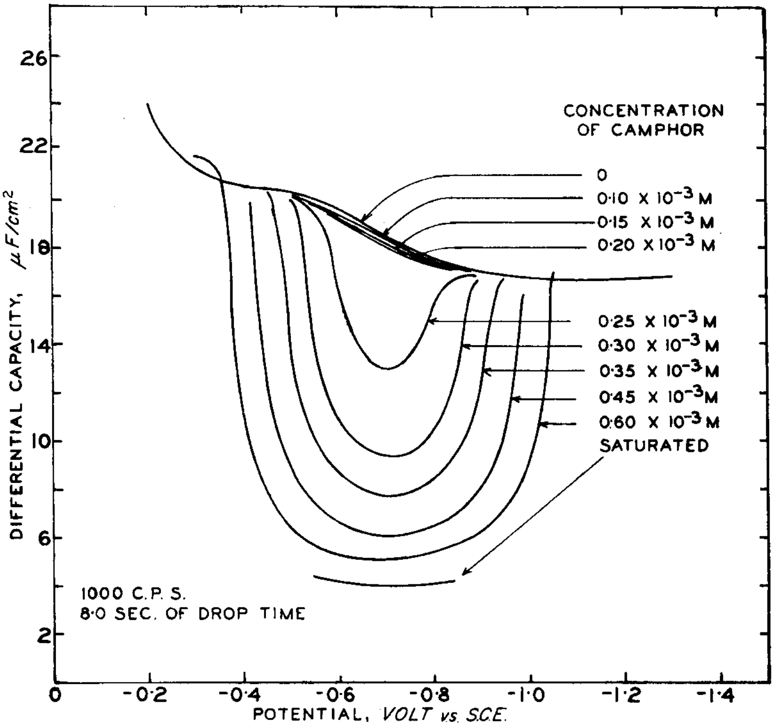

Fig. 1.—Differential capacity in the presence of camphor.

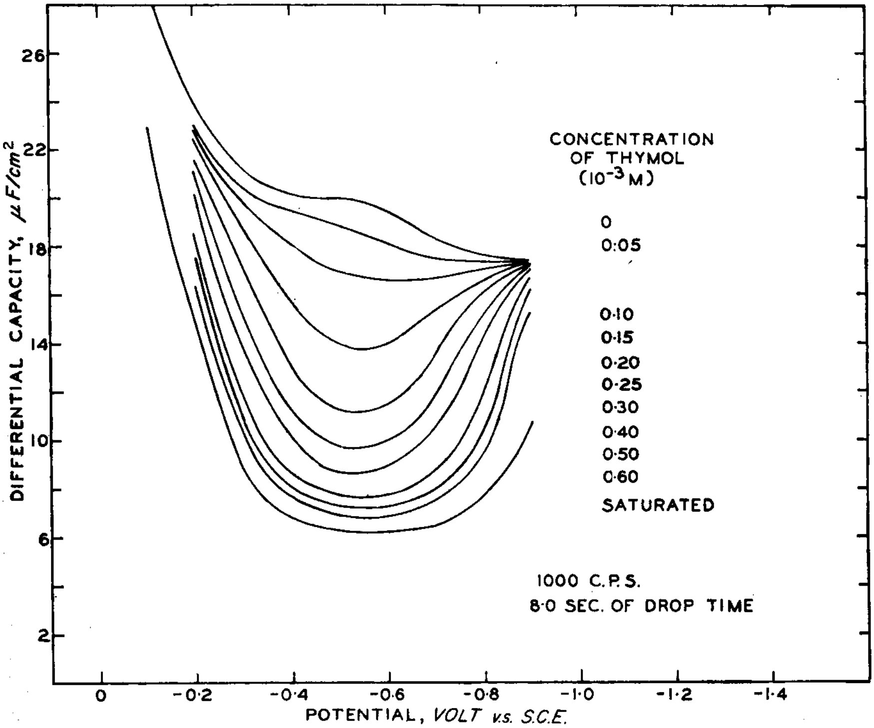

Fig. 2.—Differential capacity in the presence of thymol.

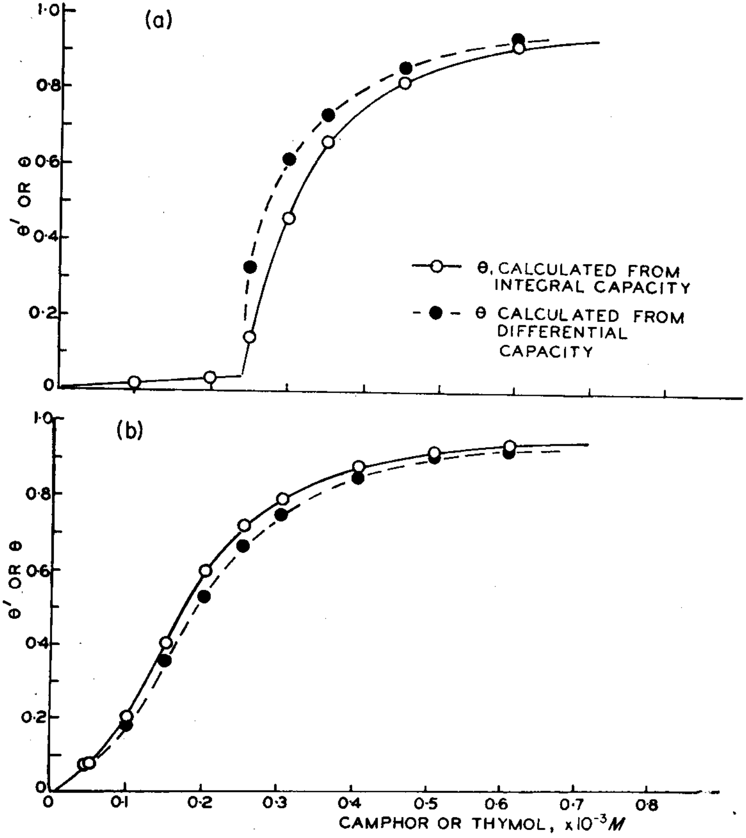

Fig. 3a.—Surface coverage *vs*. concentration of camphor.
Fig. 3b.—Surface coverage *vs*. concentration of thymol.

Table I.—Double layer capacity and surface coverage as a function of concentration of surfactant at −0·64 V *vs*. S.C.E.

C, differential capacity; *K*, integral capacity;
θ′, coverage calculated from differential capacity;
θ, coverage calculated from integral capacity.

	Camphor				Thymol			
Conc., *mM*	*C* μ*F. cm*$^{-2}$	*θ′*	*K* μ*F. cm*$^{-2}$	*θ*	*C* μ*F. cm*$^{-2}$	*θ′*	*K* μ*F. cm*$^{-2}$	*θ*
0·00	19·0	0·00	19·7	0·00	19·0	0·00	19·5	0·00
0·05	—	—	—	—	18·1	0·07	18·4	0·08
0·10	18·8	0·01	19·5	0·01	16·7	0·18	16·7	0·20$_5$
0·15	18·7	0·02	19·4	0·02	14·5	0·36	14·0	0·41
0·20	18·5	0·03	19·3	0·03	12·2	0·54	11·5	0·60
0·25	14·1	0·33	17·6	0·14	10·4	0·67$_5$	9·9	0·72
0·30	9·9	0·61	14·3	0·46	9·3$_5$	0·76	8·8$_5$	0·80
0·35	8·1$_5$	0·73	9·4	0·66	—	—	—	—
0·40	—	—	—	—	8·0	0·86$_5$	7·6$_5$	0·89
0·45	6·2	0·86	7·0	0·82	—	—	—	—
0·50	—	—	—	—	7·5	0·91	7·2	0·92
0·60	5·1	0·93$_5$	5·4	0·92	7·1	0·94	6·8	0·95
Sat.	4·2	1·00	4·2	1·00	6·2	1·00	6·2	1·00

performed graphically between the redox potential and the e.c.m. potential of the blank solution. The latter was estimated as —0·52 V from the potential dependence of the drop time. The differential capacity at 1,000 cycles was used for the integration because the frequency dispersion of the capacity at —0·64 V over the range 200–5,000 cycles was less than 3 % with all of the concentrations of the surfactant solution. In Fig. 4, the differential capacity has been plotted against the coverage calculated from the integral capacity. It can be seen that the error caused by using differential capacity calculations is not much in the case of thymol, as expected.

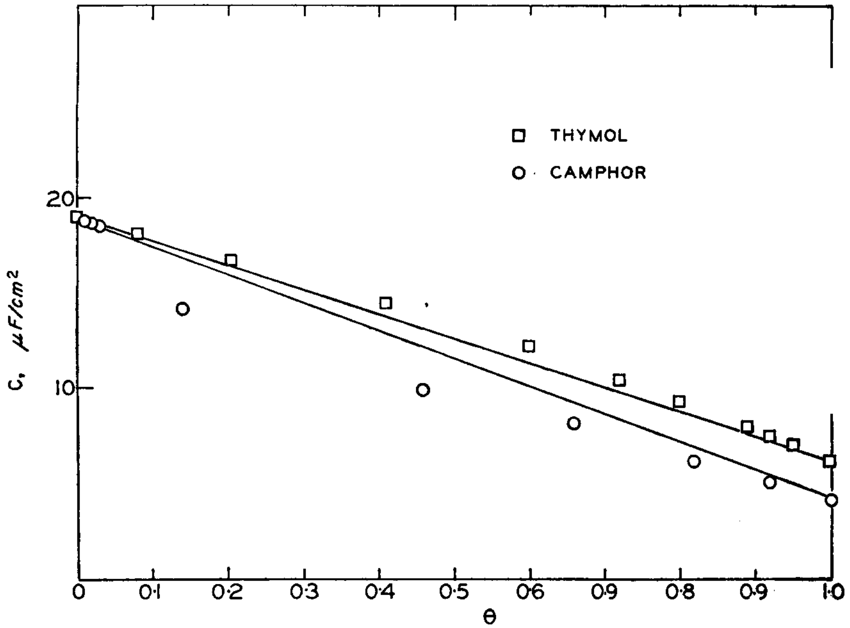

FIG. 4.—Differential capacity *vs.* coverage calculated from integral capacity.

At camphor concentrations less than 0·35 mM, the measured double layer capacity per unit of electrode area decreased slightly during drop growth. The maximum rate of decrease at —0·64 V was observed at a concentration of 0·25 mM, where the value decreased from 16·0 μF. cm^{-2} at 2-sec drop age to 14·0 μF. cm^{-2} at 8-sec drop age. This indicates that adsorption equilibrium had not quite been attained during growth.

Determination of rate constants by voltage-step method

In the absence of surfactant, the Ti^{IV}/Ti^{III} couple had the following kinetic parameters: the standard rate constant $k = 1{\cdot}7_2 \pm 0{\cdot}05 \times 10^{-3}$ cm. sec^{-1} at $0{\cdot}63_5$ V *vs.* S.C.E. and the cathodic transfer coefficient $\alpha = 0{\cdot}48$. The number of electrons transferred at the rate-determining step has been assumed as unity. In Figs. 3, 5 and 6, the rate constant and the differential double-layer capacity at the redox potential have been plotted against the concentration of the surfactant. The effect of the adsorption on the rate constant appears quite similar to that on the capacity.

Figs. 7 and 8 show a relationship between the rate constant and the coverage θ. A few points plotted against θ are also included in these figures for comparison.

Taking various complications and difficulties associated with those determinations

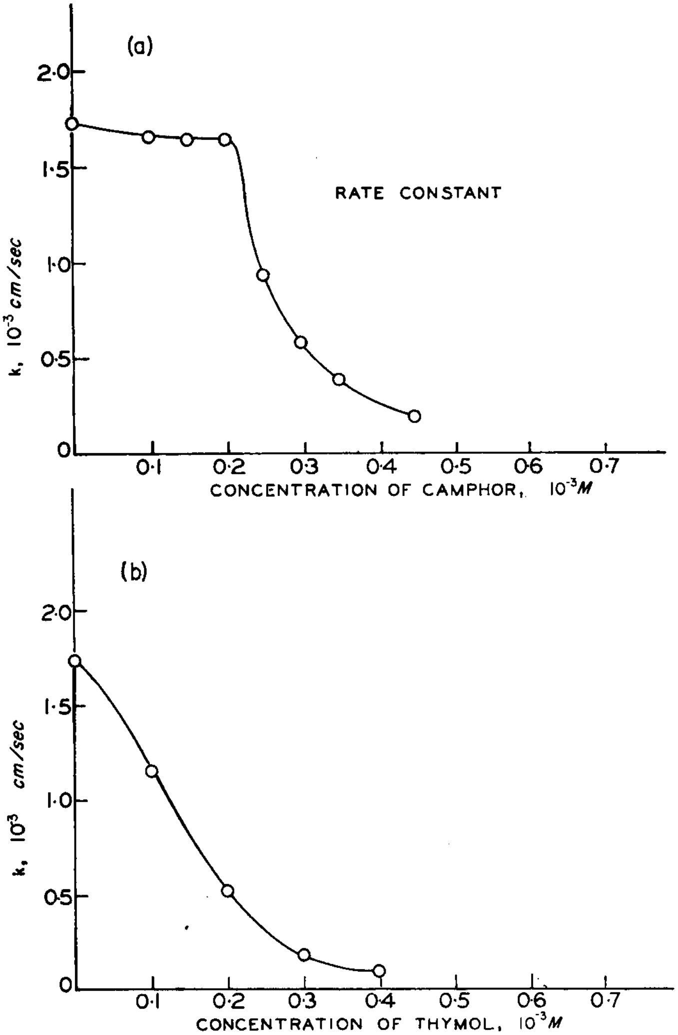

FIG. 5a.—Differential capacity *vs.* concentration of surfactant (camphor) at 0·64 V.
FIG. 5b.—Rate constant *vs.* concentration of surfactant (camphor).

into account, the change of the rate constant can be considered as linear with respect to θ in both cases. Thus, $k = k_1(1 - \theta) + k_2\theta$, where k_1 and k_2 are the rate constants of bare and of fully covered surface, respectively, the latter being estimated with thymol as less than 10^{-9} cm. sec^{-1} from d.c. current measurements.

Determination of rate constants by impedance method

The faradaic impedance at an electrode-solution interface of an electrochemical reaction can be represented by a series combination of a capacitance, C_F, and a resistance, R. In the case where the concentration of the oxidised form is equalised to that of the reduced form, the two components of the impedance are expressed by the equations[14–17]

$$R_F = \frac{RT}{n^2F^2AC}\left[\frac{1}{k_s} + \left(\frac{2}{\omega D}\right)^{1/2}\right] \tag{1}$$

and

$$\frac{1}{\omega C_F} = \frac{RT}{n^2F^2AC}\left(\frac{2}{\omega D}\right)^{1/2} \tag{2}$$

where k_s is the heterogeneous rate constant of the reaction, ω is the angular frequency of a.c. employed, C and D are the concentration and the diffusion coefficient, respectively, of the ion, and A is the area of the electrode surface. R, T, F and n have the usual significance.

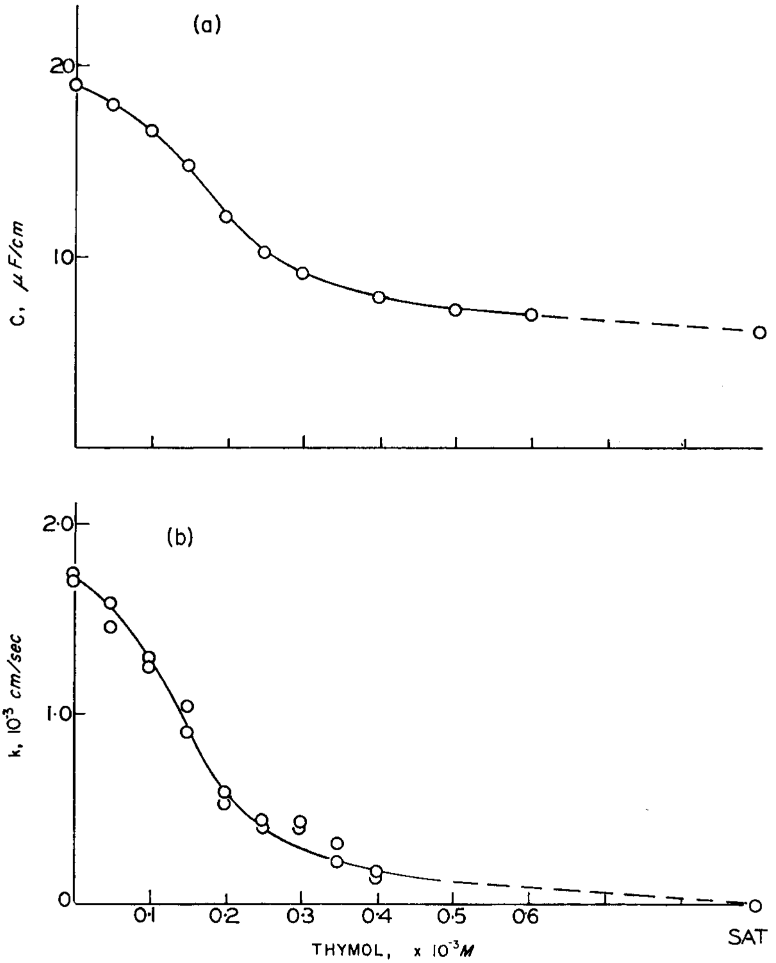

FIG. 6a.—Differential capacity at 0·64 V *vs.* concentration of surfactant (thymol).
FIG. 6b.—Rate constant *vs.* concentration of surfactant (thymol).

Observation of equations (1) and (2) shows that a plot of the faradaic reactance, $1/\omega C_F$ against $\omega^{-1/2}$ should lie on a straight line which extrapolates to the origin; and that a corresponding plot of the faradaic resistance, R_F, should lie on another straight line which is parallel to the reactance line. The rate constant, k_s, can be calculated from the vertical distance between the two lines.

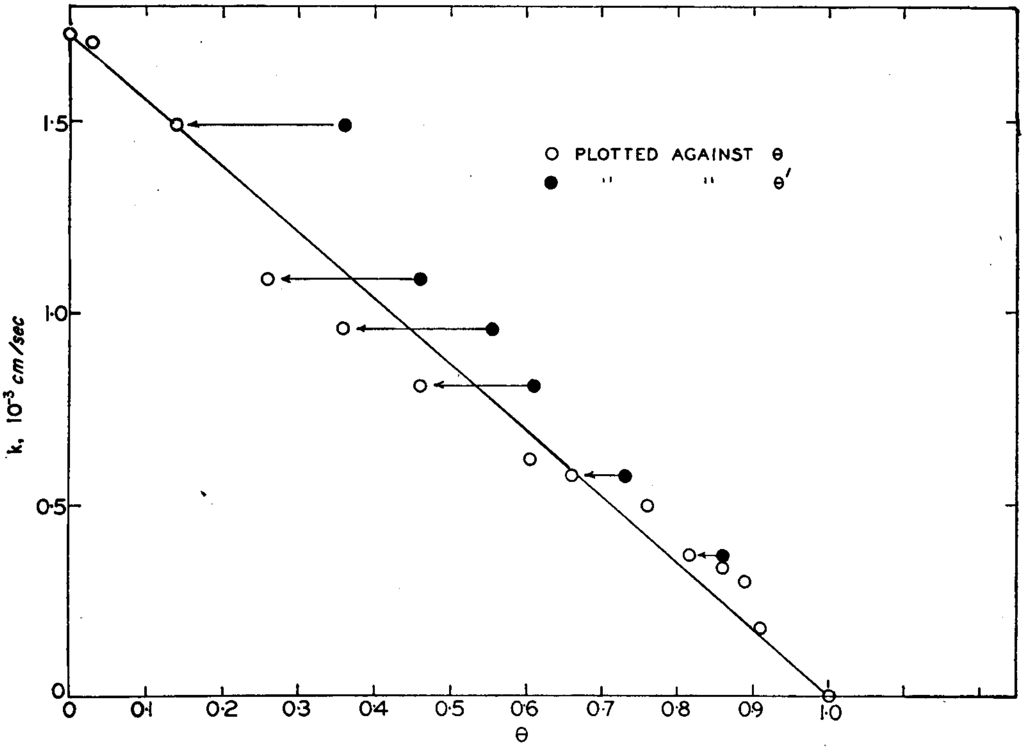

FIG. 7.—Rate constant *vs.* surface coverage (camphor).

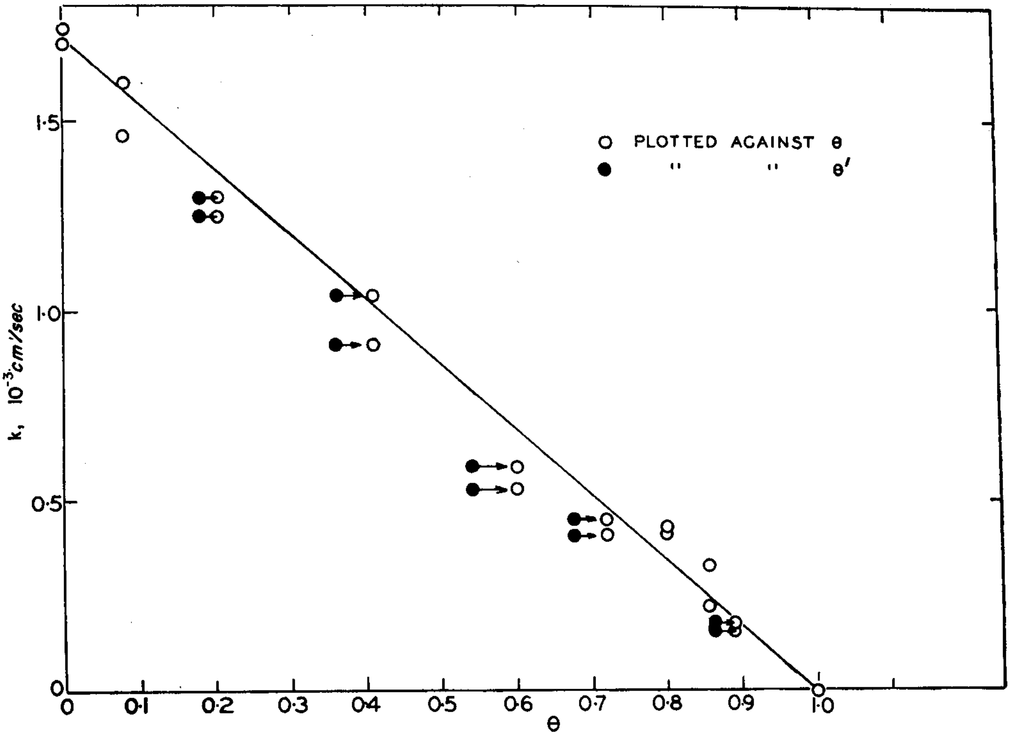

FIG. 8.—Rate constant *vs.* surface coverage (thymol).

First, the over-all impedance across the solution and the solution-mercury interface, in the presence of the titanium couple, was assumed to be represented by the equivalent circuit as shown in Fig. 9.[5,14–18] Calculation for the faradaic resistance and reactance can be performed by either the numerical[18] or vector diagram[14] method.

Values of R_s, the ohmic resistance of solution, and C_{dl}, the capacity of double layer, were supplied by the experiment for differential capacity, which had been determined with a.c. of 1,000 cps applied to the blank solution.

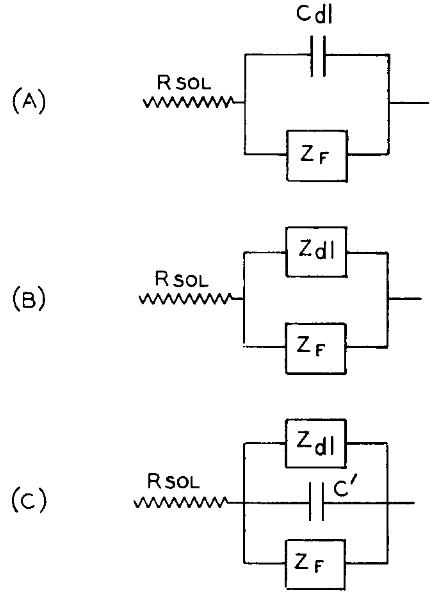

FIG. 9.—Equivalent circuits of electrode impedance.

The calculated values of the faradaic resistance, R_F, and the faradaic reactance, $1/\omega C_F$, were plotted against $\omega^{-1/2}$. The plots never lay on two parallel straight lines as postulated by equations (1) and (2). Instead two curved lines were obtained, and the vertical distance between these lines decreased with an increase of frequency. This was a trend common to all the results.

The blank solution was carefully re-examined to determine whether the equivalent circuit shown in Fig. 9A is consistent with the actual case. The results obtained by employing various frequencies revealed that the matched values of resistance increased at lower frequencies, especially in the higher concentration range of surfactants, while the values of capacitance remained almost constant regardless of frequency. The observed values of resistance in the blank solution were extrapolated to infinite frequency to obtain the resistance of the solution, R_{sol}. Then each resistance subtracted by R_{sol} can be considered as the resistance of the double layer. When the surfactants were either absent or in small concentrations, the resistance of the double layer was so small that it could reasonably be ignored in the calculations. But when the concentration of the surfactants were relatively large, the contribution of the resistance reached at most 2% of the corresponding reactance in magnitude and was no longer negligible.

A. *Double layer as a complex impedence:* To represent the double layer in the presence of adsorbed material Grahame[5] proposed an equivalent circuit consisting of a capacitance in series with a parallel combination of capacitance and resistance. The experimental values of capacitance, C_s, and resistance, R_s, represented as a series combination, are given for several concentrations of thymol in Table II. The resistance represents the excess over the solution resistance (330 Ω) extrapolated to infinite frequency, the same value being observed in the absence or presence of surfactant. Because the capacitance, C_s, remains almost constant with frequency while the excess resistance, R_s, is strongly dependent on frequency, it is qualitatively apparent that the Grahame equivalent circuit must consist of a relatively small capacitance, C_T, in series with a parallel combination of a relatively large capacitance C_3, and a large resistance, R_3. By trial and error, the components C_T, C_3 and R_3 were chosen to give the representation of R_s and C_s, as shown in Table II. The effect of increasing thymol concentration is to decrease C_T, the "pure" capacitance, more rapidly than C_3, the frequency-dependent capacitance. The parallel resistance R_3 goes through a minimum at an intermediate thymol concentration ($0{\cdot}4 \times 10^{-3}M$), corresponding to a maximum in the observed series resistance R_s. The reason for this behaviour is not clear, but it leads to complications in subtracting the double-layer admittance in calculating the rate constant of the electrode process.

TABLE II—COMPONENTS OF THE DOUBLE-LAYER IMPEDANCE

Conc. of thymol, $10^{-3}M$		cps.	R_s, Ω		C_s, μF	
			obs.	calc.	obs.	calc.
0·2	$C_T = 0{\cdot}15\ \mu F$	200	90	120	0·136	0·138
	$C_3 = 1{\cdot}6\ \mu F$	400	40	32	0·136	0·137
	$R_3 = 1{\cdot}9\ K$	600	18	15	0·137	0·137
		1000	14	6	0·137	0·137
0·4	$C_T = 0{\cdot}10$	200	180	240	0·092	0·094
	$C_3 = 1{\cdot}3$	400	65	70	0·093	0·093
	$R_3 = 1{\cdot}25$	600	40	35	0·094	0·093
		1000	20	14	0·094	0·093
0·6	$C_T = 0{\cdot}09$	200	120	175	0·083	0·084
	$C_3 = 1{\cdot}2$	400	54	54	0·084	0·084
	$R_3 = 2{\cdot}0$	600	25	25	0·085	0·084
		1000	18	10	0·085	0·084

Faradaic resistance and reactance were calculated by the vector-diagram method, using the complex admittance, in place of mere capacitive admittance of the double layer. The calculated values, however, gave only small increases to the plots for both components. Hence, the resulting curves were not remarkably improved.

B. *Introducing an additional capacitance*: Assuming that the double layer capacity might change its magnitude between the blank solution and the solution containing titanium, an equivalent circuit was considered which included an additional capacity parallel to the impedance of double layer (C in Fig. 9).

The magnitude of the capacitance was empirically chosen so that the resistive and the reactive components of the faradaic impedance were as close to those postulated by equations (1) and (2) as possible. The vector-diagram method was adopted for the calculation.

By choosing a suitable capacitance, both the resistance and the reactance lines became almost straight and parallel to each other, and the latter lines could be extrapolated to the origin. The values of the additional capacitance are tabulated in Tables III and IV, where they are also compared with the differential capacity measured at 1,000 cps. The improvement is marked by thus introducing an additional capacitance.

TABLE III—EFFECT OF CAMPHOR

Concentration of camphor, $10^{-3}M$	C', Capacity subtracted $\mu F/cm.^2$	C', Capacity subtracted % to C_{dl} at 1000 cps	Slope, $10^3\ \Omega\ sec^{-1/2}$	D(apparent), $10^{-6}\ cm.^2\ sec^{-1}$	k_s, $10^{-3}\ cm.\ sec^{-1}$
0	2·50	13·1	7	1	1·7$_3$
0·10	1·88	9·9	10	0·5	1·6$_6$
0·15	1·66	8·8	11	0·4	1·6$_5$
0·20	1·63	8·7	12	0·3	1·6$_5$
0·25	0	0	15	0·2	0·9$_4$
0·30	0·29	2·9	48	0·02	0·5$_9$
0·35	0·43	5·3	70	0·01	0·3$_9$
0·45	0·29	4·6	125	0·003	0·2$_0$

TABLE IV—EFFECT OF THYMOL

Concentration of thymol, $10^{-3}M$	C', Capacity subtracted $\mu F/cm^2$	C', Capacity subtracted % to C^{dl} at 1000 cps	Slope, $10^3\ \Omega\ sec^{-1/2}$	D(apparent), $10^{-6}\ cm.^2\ sec^{-1}$	k_s, $10^{-3}\ cm.\ sec^{-1}$
0	2·47	12·9	8	0·5	1·7$_4$
0·10	3·26	19·6	12	0·2	1·1$_6$
0·20	2·47	20·1	38	0·02	0·5$_2$
0·30	1·68	16·8	100	0·002	0·1$_8$
0·40	1·13	13·6	650	(8×10^{-5})	0·0$_9$

The effect of this additional admittance may be interpreted as a rapid electron exchange between the adsorbed reactants and the electrode, such as that postulated by Laitinen and Randles[18] for a cobalt^{III}/cobalt^{II} system.

C. *Reaction rate*: Estimated values of R_F and $1/\omega C_F$ for various concentrations of the surfactants, camphor and thymol, were plotted against $\omega^{-1/2}$. Fig. 10, which is an example of the plots, illustrates the variation of both R_F and $1/\omega C_F$ with the increasing concentration of camphor.

Rough estimation of the apparent diffusion coefficient of the titanium ion is possible from the slopes of each pair of corresponding lines. Values of slopes and, hence, the diffusion coefficient are shown in Tables III and IV in the presence of camphor and thymol, respectively. The large decrease of apparent diffusion coefficient observed at high surface coverages cannot be attributed to a change of diffusion rate in solution because the polarographic diffusion current is not appreciably affected even by high concentrations of camphor or thymol. It might be regarded, however, as evidence for a slow penetration step of a nearly saturated surface layer. Further experimental work on this point is desirable.

Vertical distances between corresponding resistance and reactance lines permit

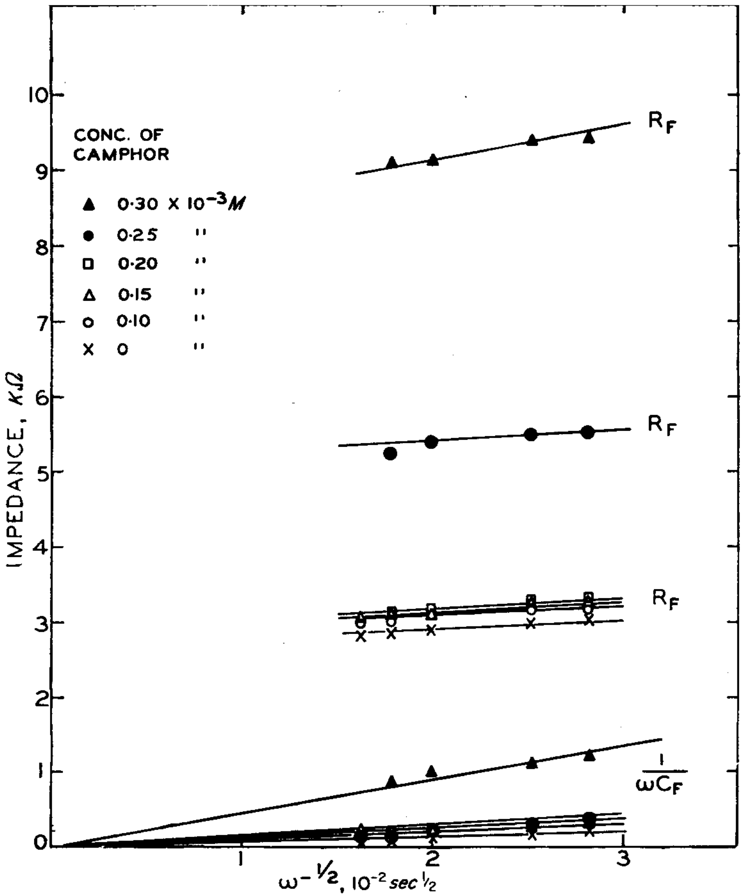

FIG. 10a.—Faradaic resistance, R_F and reactance, $1/\omega C_F$, in the presence of camphor.

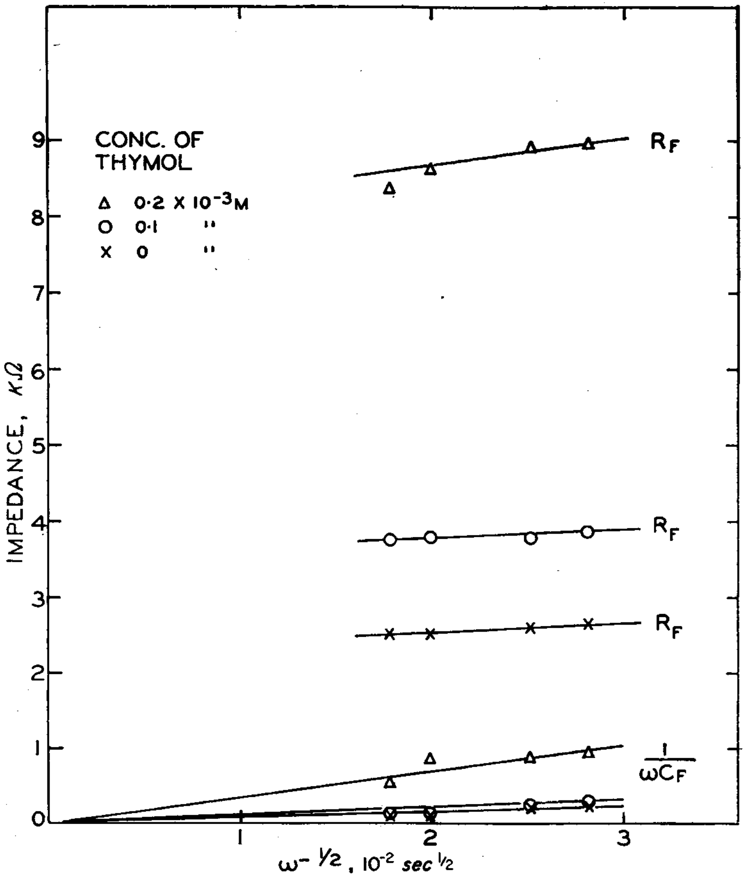

FIG. 10b.—Faradaic resistance, R_F and reactance, $1/\omega C_F$, in the presence of thymol.

the reaction rate constants to be calculated, the values also being tabulated. Experiments had been extended to the saturating concentrations of camphor and thymol, but the extremely small values of capacitance gave rise to intolerable errors in calculation; therefore, these results have been neglected here.

The observed value of the rate constant, $1{\cdot}7 \times 10^{-3}$ cm. sec^{-1}, in the absence of surfactants is in good agreement with that obtained by the voltage-step method. This is smaller than either 9×10^{-3} by Randles and Somerton[20] or 5 or $3{\cdot}5 \times 10^{-3}$ by Delahay and Trachtenberg[21] obtained by the impedance method. Because the experimental condition of the former was not described and the latter was obtained in a solution containing sodium chloride, an exact comparison is difficult to make.

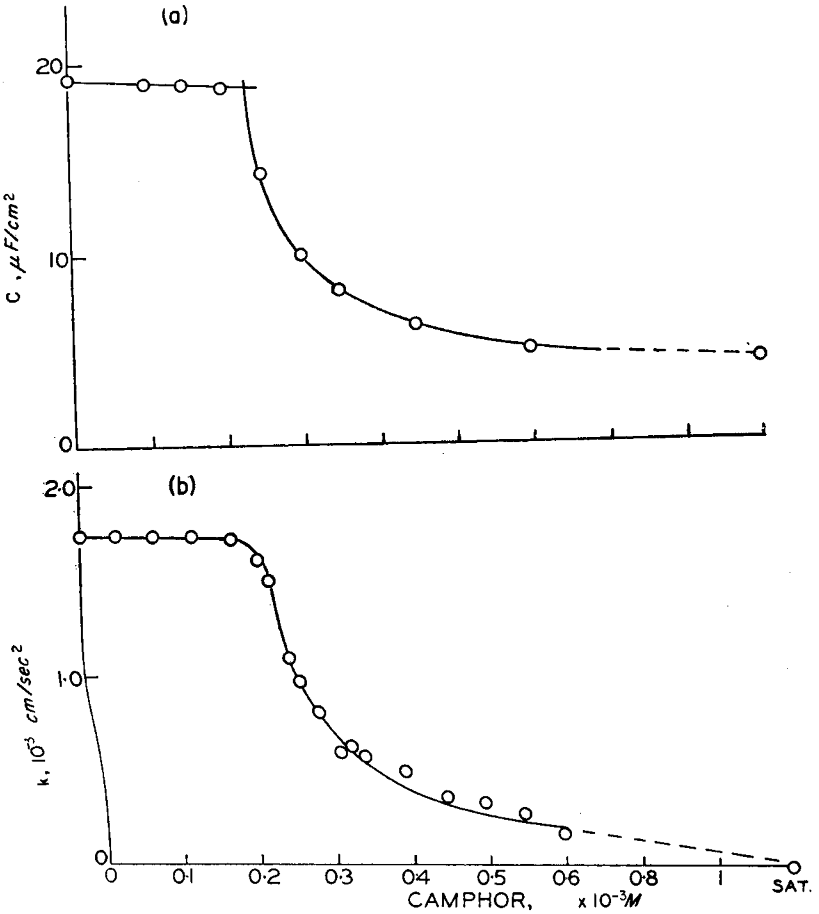

FIG. 11a.—Effect of camphor on electrode reaction of Ti.
FIG. 11b.—Effect of thymol on electrode reaction of Ti.

The rate constant decreases rapidly in the presence of thymol, and is reduced to one-tenth of the original value at the concentration of thymol $0{\cdot}3 \times 10^{-3}M$. On the other hand, camphor exerts almost no inhibiting effect up to $0{\cdot}2 \times 10^{-3}M$, then exerts a serious effect, the rate constant being about one-tenth of the original value at $0{\cdot}45 \times 10^{-3}M$. These effects on the rate constant are shown in Fig. 11.

Comparison of voltage-step and impedance methods

For a simple electrode reaction, the voltage-step and impedance methods may be said to be equivalent, but for the determination of rate constants greater than 10^{-2} cm. sec^{-1} the impedance method is usually more accurate.[22]

In the present case, however, the voltage-step method has advantages which led to more reliable values for rate constants in the presence of adsorbed organic materials. The essential difficulty in interpreting impedance results arises from complications in subtracting out the admittance of the blank. First, the frequency dependence of resistance and capacitance observed in the presence of an adsorbed layer means that the double layer can no longer be represented as a simple capacitance but a capacitance shunted by a resistance, as has previously been shown by Grahame.[5] In the present investigation, it has been shown that this is a relatively minor complication, but undoubtedly it leads to additional scatter in the calculated rate constants. Second, the abnormally great Warburg impedance observed in the presence of adsorbed materials especially at high surface coverages needs further study. The uncertainty from this correction appears to be more serious, and would probably be encountered whenever adsorbed phases are present. Third, a specific effect encountered in the present problem is that of adsorption of electroactive species. Although this effect may not always be observed, it has led in the present case to further uncertainties in the rate constant calculated from impedance values.

In the voltage-step method, the total period of time during which a current was recorded was usually less than 300 μsec. Thus, all observations in this study would correspond to bridge measurements at high frequencies (several kilocycles per sec). The frequency dispersion of double-layer capacity becomes unimportant at high frequencies. Moreover, the abnormal Warburg admittance becomes relatively less important at high frequencies because it approaches zero at infinite frequency. Finally, the effect of adsorbed electroactive species appears as an abnormally large double-layer capacitance, which is subtracted out automatically in the extrapolation procedure. This latter statement is true only if the adsorbed species undergo sufficiently rapid electron exchange that their effect can be represented by a pure capacitance. A slow electron exchange of adsorbed species would give rise to a capacitance in series with a resistance, which would result in an increased time constant for the reduction process as compared with the charging process.

CONCLUSIONS

The adsorption of camphor and thymol on a dropping mercury electrode was determined from capacitance measurements. A comparison was made of the electrode coverage as calculated from differential and integral double-layer capacity, and the magnitude of the error caused by using differential capacity calculations was estimated.

The standard rate constant for the titanium^{IV}-titanium^{III} couple in 1M tartaric acid, 0·2M sodium sulphate was determined in the absence of surfactant. The voltage-step method gave a value of $1{\cdot}72 \times 10^{-3}$ cm. sec^{-1}, and the impedance method gave 1·73 and $1{\cdot}74 \times 10^{-3}$ cm. sec^{-1}.

The voltage-step method proved simpler than the impedance method in the presence of surfactant. To interpret the impedance method, it was necessary to introduce an empirical correction in the form of an additional capacitative admittance in parallel with the usual Warburg admittance. This correction arises from specific adsorption of electroactive species.

The rate constants calculated from voltage-step measurements were more reliable than those from impedance values, and showed approximately linear dependance on surface coverage, for both thymol and camphor.

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Zusammenfassung—Es ist mit Hilfe der Spannungsstufen- und Impedanzmethoden untersucht worden, wie Kampfer- und Thymolverinreinigungen an einer Quecksilberoberfläche die Geschwindigkeitskonstante der TiIV/TiIII Redoxreaktion in 1 M Weinsäure beeinflüssen. Eine spezifische Adsorption der elektronegativen Bestandteile erwies sich als Nachteil mehr bei der Impedanzmethode als bei der Spannungsstufenmethode. Die Geschwindigkeitskonstante scheint mit Oberflächenbedeckung linear abzunehmen.

Résumé—On a déterminé l'effet de la contamination d'une surface de mercure par le camphre et le thymol sur la constante de vitesse normale de demi-réaction du système titane(IV)-titane(III) en acide tartrique 1 M, au moyen des méthodes par incrément de potentiel et d'impédance. Les complications dues à l'adsorption spécifique des espèces électroactives sont plus perturbatrices avec la méthode d'impédance qu'avec la méthode par incrément de potentiel. On indique une décroissance linéaire de la constante de vitesse avec l'étendue de la surface.

REFERENCES

[1] P. Delahay, *Progress in Polarography*, Vol. I, Ed. by P. Zuman and I. M. Kolthoff. John Wiley and Sons, New York, 1962, p. 65.
[2] C. N. Reilley and W. Stumm, *ibid*, p. 81.
[3] A. N. Frumkin, *Transactions of the Symposium on Electrode Processes*, Ed. by E. Yeager, John Wiley and Sons, New York, 1961, p. 1.
[4] J. Kuta, *Review of Polarography*, 1963, **11**, 62.
[5] D. C. Grahame, *J. Amer. Chem. Soc.*, 1946, **68**, 301.
[6] D. K. Roe, Ph.D. Thesis, University of Illinois, 1959.
[7] H. A. Laitinen, R. Tischer and D. K. Roe, *J. Electrochem. Soc.*, 1960, **107**, 546.
[8] B. Mosier, Ph.D. Thesis, University of Illinois, 1957.
[9] E. O. Sherman, Ph.D. Thesis, University of Illinois, 1962.
[10] D. C. Grahame, *J. Amer. Chem. Soc.*, 1949, **71**, 2975.
[11] W. Vielstich and P. Delahay, *ibid.*, 1957, **79**, 1874.
[12] M. Breiter and P. Delahay, *ibid.*, 1959, **81**, 2938.
[13] A. N. Frumkin, *Z. Physik*, 1926, **35**, 792.
[14] J. E. B. Randles, *Disc. Faraday Soc.*, 1947, **1**, 11.
[15] B. Ershler, *ibid.*, 1947, **1**, 269; *J. Phys. Chem. U.S.S.R.*, 1948, **22**, 683.
[16] H. Gerischer, *Z. Physik. Chem.*, 1951, **198**, 286.
[17] D. C. Grahame, *J. Electrochem. Soc.*, 1952, **99**, 370C.
[18] H. A. Laitinen and J. E. B. Randles, *Trans. Faraday Soc.*, 1955, **51**, 54.
[19] P. Delahay and T. J. Adams, *J. Amer. Chem. Soc.*, 1952, **74**, 5740.
[20] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, 1952, **48**, 937.
[21] P. Delahay and I. Trachtenberg, *J. Amer. Chem. Soc.*, 1958, **80**, 2094.
[22] J. E. B. Randles, *Progress in Polarography*, Ed. by P. Zuman and I. M. Kolthoff, Chapter VI. John Wiley and Sons, New York. 1962.

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CHRONOPOTENTIOMETRIC STUDY OF THALLIUM^{I} ION IN GLACIAL ACETIC ACID†

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Summary—The thallous ion-thallium amalgam system has been studied chronopotentiometrically in glacial acetic acid (HAc) as a solvent, using 0·25*M* ammonium acetate as supporting electrolyte. The transition time relationships between the cathodic transition time and the first anodic transition time on current reversal were verified. Analogous studies were carried out at the thallium amalgam electrode, determining the anodic transition time and the cathodic transition time on current reversal. The predicted potential-time relationships for the above-mentioned chronopotentiometric processes were verified, and it was established that the thallous acetate-thallium amalgam couple is reversible with the formal potential of 0·347 ± 0·005 V *vs.* the saturated aqueous calomel electrode. The diffusion coefficients of thallous ion and thallium in mercury were found to be identical, $4{\cdot}3 \times 10^{-6}$ cm^2. sec^{-1}.

INTRODUCTION

VARIOUS investigators[1–17] have obtained solutions for a number of simple and complex problems arising in chronopotentiometry. The present work is concerned with the verification of the predicted relationships between concentration and transition time, and between potential and time, for the thallous acetate—thallium amalgam couple, using 0·25*M* ammonium acetate supporting electrolyte in acetic acid (HAc) as solvent. Studies reported below include the reduction of thallous acetate into a mercury pool or thallium amalgam, followed by current reversal at the first cathodic transition time; and oxidation of thallium from thallium amalgam followed by current reversal at the first anodic transition time.

Table I summarises the surface concentrations of thallous ion, $C_O{}^s$, and thallium amalgam, $C_R{}^s$, which will result at time, t, after the start of reduction before the first cathodic transition time, τ_c, and between the first cathodic transition time and the subsequent anodic transition time, τ_a', on current reversal at $t = \tau_c$,[12]

where
$$\tau_c = \frac{n\mathscr{F}(\pi D_O)^{\frac{1}{2}}}{2i_O} C_O{}^o,$$

D_O and $C_O{}^o$ represent the diffusion coefficients and bulk concentrations of the oxidised species, respectively, i_O is the absolute value of constant current density, and τ_a' is the time lapse between the cathodic transition time and the anodic transition time. Analogous relations are given for the case where the initial process is an oxidation, resulting first in an anodic transition time, τ_a,

where τ_a
$$= \frac{n\mathscr{F}(\pi D_R)^{\frac{1}{2}}}{2i_O} C_R{}^o,$$

followed by cathodic transition time, τ_c', on current reversal at $t = \tau_a$.[12]

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† Taken in part from the Ph.D. Thesis of T. O. Rouse.

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TABLE I.—SURFACE CONCENTRATIONS DURING CONSTANT CURRENT ELECTROLYSIS FOLLOWED BY CURRENT REVERSAL AT FIRST TRANSITION TIME†[12]

Initial Process	Before first transition time		Between first and second transition times	
	C_O^s	C_R^s	C_O^s	C_R^s
Reduction	$k_O\{\tau_c^{\frac{1}{2}} - t^{\frac{1}{2}}\}$ $(t \leq \tau_c)$	$k_R\{\tau_a^{\frac{1}{2}} + t^{\frac{1}{2}}\}$ $(t \leq \tau_c)$	$k_O\{\tau_c^{\frac{1}{2}} + 2(t - \tau_c)^{\frac{1}{2}} - t^{\frac{1}{2}}\}$ $(\tau_c < t \leq \tau_c + \tau_a')$	$k_R\{\tau_a^{\frac{1}{2}} - 2(t - \tau_c)^{\frac{1}{2}} + t^{\frac{1}{2}}\}$ $(\tau_c < t \leq \tau_c + \tau_a')$
Oxidation	$k_O\{\tau_c^{\frac{1}{2}} + t^{\frac{1}{2}}\}$ $(t \leq \tau_a)$	$k_R\{\tau_a^{\frac{1}{2}} - t^{\frac{1}{2}}\}$ $(t \leq \tau_a)$	$k_O\{\tau_c^{\frac{1}{2}} - 2(t - \tau_a)^{\frac{1}{2}} + t^{\frac{1}{2}}\}$ $(\tau_a < t \leq \tau_a + \tau_c')$	$k_R\{\tau_a^{\frac{1}{2}} + 2(t - \tau_a)^{\frac{1}{2}} - t^{\frac{1}{2}}\}$ $(\tau_a < t \leq \tau_a + \tau_c')$

† For the reduction (or oxidation) of one soluble species to another where

$$k_O = \frac{2i_O}{n\mathscr{F}(\pi D_O)^{\frac{1}{2}}}$$

$$k_R = \frac{2i_O}{n\mathscr{F}(\pi D_R)^{\frac{1}{2}}}$$ and i_O = absolute value of current density.

If the first electrode process is a reduction, the relationship between the first cathodic transition and the anodic transition time occurring on current reversal is

$$[\tau_c + \tau_a']^{\frac{1}{2}} + \tau_a^{\frac{1}{2}} = 2[\tau_a']^{\frac{1}{2}}, \tag{1}$$

while if the initial process is an oxidation, the analogous relation is

$$[\tau_a + \tau_c']^{\frac{1}{2}} + \tau_c^{\frac{1}{2}} = 2[\tau_c']^{\frac{1}{2}}. \tag{2}$$

The potential-time curves for the reversible electrode process are obtained by substituting the surface concentrations given in Table I into equation (3a)

$$E = E^* + \frac{RT}{n\mathscr{F}} \ln \frac{C_O^s D_O^{\frac{1}{2}}}{C_R^s D_R^{\frac{1}{2}}}, \tag{3a}$$

where E^* is the observed potential when $C_O^s D_O^{\frac{1}{2}} = C_R^s D_O^{\frac{1}{2}}$. In the case under consideration, E^* is identical with the polarographic half-wave potential and the chronopotentiometric quarter-wave potential, *i.e.*,

$$E^* = E^\circ + \frac{RT}{n\mathscr{F}} \ln \frac{f_O D_R^{\frac{1}{2}}}{f_R D_O^{\frac{1}{2}}}, \tag{3b}$$

where E° is the standard potential for Ox. + $n\varepsilon$ = Red. and f represents the activity coefficient of the species indicated in the subscript. We call E^* the "characteristic potential". This characteristic potential occurs at a time, t^*, the "characteristic time". Relationships for the various cases are given in Table II. If the first electrode process

TABLE II.—CHARACTERISTIC TIMES, t^*

Initial process	Before first transition time	Between first and second transition times
Reduction	$0{\cdot}5(\tau_c^{\frac{1}{2}} - \tau_a^{\frac{1}{2}}) = t^{*\frac{1}{2}}$ observed only if $\tau_c > \tau_a$	$4(t^* - \tau_c)^{\frac{1}{2}} - 2(t^*)^{\frac{1}{2}} = \tau_a^{\frac{1}{2}} - \tau_c^{\frac{1}{2}}$ always observed
Oxidation	$0{\cdot}5(\tau_a^{\frac{1}{2}} - \tau_c^{\frac{1}{2}}) = t^{*\frac{1}{2}}$ observed only if $\tau_a > \tau_c$	$4(t^* - \tau_a)^{\frac{1}{2}} - 2(t^*)^{\frac{1}{2}} = \tau_c^{\frac{1}{2}} - \tau_a^{\frac{1}{2}}$ always observed

is a reduction and $C_R{}^0 = 0$, then $\tau_a = 0$ and the first current reversal relationship given in Table II reduces to a result previously obtained by Berzins and Delahay.[3]

EXPERIMENTAL

Apparatus

The constant current source, high impedance amplifier and recorders used in this study are described elsewhere.[12] The chronopotentiometric cell used was similar to that used by Delahay[18] with the following differences: (1) The plug was machined from Teflon instead of from Lucite. (2) The entire cell body was jacketed with water and maintained at 25° ± 0·2° by circulating water from a thermostat. (3) The Lugen capillary was sealed through the side of the cell to fix the position of the tip of the salt bridge with respect to the mercury pool. The diameter of the hole in the Teflon plug was 1·630 cm, and exactly the same volume of mercury was delivered to the plug in all the experiments to ensure a constant distance between the tip of the salt bridge and the mercury surface. The effective electrode area was determined by a procedure which will be reported elsewhere.

Reagents

Reagent-grade chemicals were used in all cases.

Glacial acetic acid was purified by boiling with anhydrous chromic oxide, followed by azeotropic distillation with excess benzene to remove water, in turn followed by careful fractionation.

0·25M Ammonium acetate: Reagent-grade ammonium acetate was dissolved in the purified HAc. The water content of the supporting electrolyte used was found to be 0·1% by Karl Fischer titration.

Thallium amalgams were prepared *in situ* in the chronopotentiometric cell by constant-current electrolysis at the mercury cathode of stirred, deaerated solutions of thallous acetate in 0·25*M* ammonium acetate in HAc. The current densities chosen were such that the potential of the mercury cathode insured 100% current efficiency for the reduction of thallous ion. The concentration of the amalgams was calculated from the number of coulombs used in the electrolysis and the known volume of the mercury cathode.

Thallium acetate: A standard thallium acetate solution was prepared by solution of an appropriate amount of thallium formate in water followed by precipitation with sodium carbonate. The resulting carbonate was recrystallised several times from water, washed and dried. A weighed amount of this carbonate was dissolved in the ammonium acetate supporting electrolyte. The amount of water formed in this process is negligible compared with the total amount of water in the electrolyte.

All potentials were measured against the saturated aqueous calomel electrode. An intermediate salt bridge containing the acetic acid supporting electrolyte present in the chronopotentiometric cell was placed between aqueous calomel electrode and the Lugen capillary.

RESULTS AND DISCUSSION

The reaction

$$\mathrm{Tl}^{(1)} + \varepsilon + \mathrm{Hg} \rightleftharpoons \mathrm{Tl(Hg)} \tag{4}$$

was studied in 0·25*M* ammonium acetate in HAc in order to verify the relations given in Tables I and II. In such a mixture of reduced and oxidised forms, two transition time constants, J_O and J_R, may be defined in terms of relationships given in Table I. The transition time constant for the oxidised form is given by

$$J_O = \frac{i_0\tau_c{}^{\frac{1}{2}}}{C_O{}^0} = \frac{-\,i_O[(\tau_a + \tau_c')^{\frac{1}{2}} - 2(\tau_c')^{\frac{1}{2}}]}{C_O{}^0} = \frac{n\mathscr{F}(\pi D_O)^{\frac{1}{2}}}{2} \tag{5a}$$

in the case where the first electrochemical process is a reduction.

If the current is reversed at the first transition time, the transition time constant for the reduced form is given by

$$J_R = \frac{i_O\tau_a{}^{\frac{1}{2}}}{C_R{}^0} = \frac{-\,i_O[\tau_c + \tau_a')^{\frac{1}{2}} - 2(\tau_a')^{\frac{1}{2}}]}{C_R{}^0} = \frac{n\mathscr{F}(\pi D_R)^{\frac{1}{2}}}{2} \tag{5b}$$

when the initial process is an oxidation and the current is reversed at the first transition time.

TABLE III.—CHRONOPOTENTIOMETRY OF THALLOUS ION–THALLIUM AMALGAM IN HAc

Initial process	$C^{0(b)}_{Tl^+}$, mM	$C^{0(b)}_{Tl(Hg)}$, mM	$J^{(a)}_{Tl^+}$ $\frac{\mu A\ sec^{\frac{1}{2}}}{cm^2 mM}$	$J^{(a)}_{Tl(Hg)}$ $\frac{\mu A\ sec^{\frac{1}{2}}}{cm^2 mM}$	Exptl. value of $2{\cdot}303\ \frac{RT}{n\mathscr{F}}$		E^*, v	Number of determinations
					Before first transition time v	After current reversal, v		
Reduction	3·19	0·0	185 ± 3·0%	—	0·064 ± 0·002	0·060 ± 0·002	0·346 ± 0·002	24
Reduction	4·25	0·0	177 ± 2·3%	—	0·061 ± 0·001	0·058 ± 0·002	0·349 ± 0·002	26
Reduction	3·34	2·12	—	157 ± 10·6%	0·064 ± 0·005	0·070 ± 0·005	0·345 ± 0·002	16
Oxidation	3·34	2·12	177 ± 2·4%	181 ± 10·0%	0·065 ± 0·007	0·061 ± 0·003	0·343 ± 0·001	14
Oxidation	3·27	2·82	—	231 ± 9·2%	0·061 ± 0·001	0·071 ± 0·006	0·354 ± 0·002	4
Average			180 ± 2·1%	190 ± 14·7%	0·063 ± 0·003	0·064 ± 0·005	0·347 ± 0·005	

(a) See equations (5a) and (5b) for definition.

(b) C° = bulk concentration.

The results obtained with several HAc solutions containing thallous acetate at mercury and at thallium-amalgam electrodes are summarized in Table III. The values of J_{Tl^+} for the initial cathodic experiments at an amalgam electrode are omitted, because the concentration of the HAc solution, after preparation of the amalgam, was determined from the cathodic transition times and the value of J_{Tl^+} found for experiments at a mercury electrode. Current densities varied from 154 μA. cm^{-2} to 2050 μA. cm^{-2}. As is seen in Table III, the agreement between the various J values is good, and verifies the relationships between the different transition times. Also summarised in Table III are the slopes of E *vs.* log $\frac{C^s{}_{\text{Tl}^+}}{C^s{}_{\text{Tl(Hg)}}}$ where the appropriate surface concentrations given in Table I have been substituted. The slopes indicate that reaction (4) occurs reversibly in a supporting electrolyte of 0·25M ammonium acetate in HAc.

The characteristic potentials listed in Table III are corrected for the ohmic potential drop contribution which cannot be avoided in this high-resistance supporting electrolyte. The observed characteristic potential, $(E^*)_{\text{obs.}}$, is related to the actual characteristic potential by

$$(E^*)_{\text{obs.}} = E^* - iR \tag{6}$$

where R is the effective resistance between the tip of the Lugen capillary and the mercury pool. The actual characteristic potentials listed in Table III were obtained by plotting the observed characteristic potential *vs.* the current used in the particular electrolysis and extrapolating to zero current. The agreement found between the characteristic potentials is excellent, and verifies the validity of the theoretical relationship pertaining to these different situations.

In addition, potentiometric measurements (at zero current) indicate that the value of formal potential for reaction (4) is $-0{\cdot}353$ v. Because ion-pair formation must be extensive, this potential value merely represents the e.m.f. at which the ratio of the analytical concentration of thallous acetate to the thallium amalgam concentration is 1. We also find that the diffusion coefficient of thallous ion in HAc solutions of 0·25M ammonium acetate ($4{\cdot}3 \times 10^{-6}$ cm^2. sec^{-1}) equals that of thallium amalgam, therefore the observed formal potential should correspond exactly to E^*. Within the experimental error this result is found, further supporting the above conclusions.

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Zusammenfassung—Das System Thallium(I)–Thalliumamalgam wurde chronopotentiometrisch in Eisessig als Lösungsmittel mit 0,25m Ammonacetat als Leitsalz untersucht. Die Beziehungen zwischen kathodischer Transitionszeit und erster anodischer Transitionszeit bei Stromumkehr wurden verifiziert. Analoge Untersuchungen wurden an der Thalliumamalgam-elektrode durchgeführt, wobei die anodische und die kathodische Transitionszeit bei Stromumkehr bestimmt wurden. Die vorausgesagten Potential-Zeit-Beziehungen für die erwähnten chronopotentiometrischen Prozesse wurden bestätigt und es wurde festgestellt, daß das System Thalliumacetat/Thalliumamalgam reversibel ist mit einem formalen Potential von 0,347 ± 0,005 Volt gegen die gesättigte wäßrige Kalomelelektrode. Die Diffusionskoeffizienten von Thallium(I) und Thallium in Quecksilber sind gleich und betragen 4,3 . 10^{-6} cm^2/sec.

Résumé—On a étudié chronopotentiométriquement le système ion thalleux-amalgame de thallium en acide acétique glacial (HAc) comme solvant, avec de l'acétate d'ammonium 0,25 M comme électrolyte support. On a vérifié les rapports des temps de transition, entre le temps de transition cathodique et le premier temps de transition anodique, lors de l'inversion du courant. On a effectué des études analogues à l'électrode en amalgame de thallium, déterminant les temps de transition anodique et cathodique lors de l'inversion du courant. Les relations potentiel-temps prévues pour les techniques chronopotentiométriques ci-dessus ont été vérifiées et on a établi que le couple acétate thalleux-amalgame de thallium est réversible, avec le potentiel défini de 0,347 ± 0,005 volt par comparaison à l'électrode au calomel aqueux saturé. On a trouvé que les coefficients de diffusion des ions thalleux et du thallium dans le mercure sont identiques: $4{,}3 \times 10^{-6}$ cm^2/sec.

REFERENCES

[1] L. Gierst and A. L. Julliard, *J. Phys. Chem.*, 1953, **57**, 701.
[2] P. Delahay and T. Berzins, *J. Amer. Chem. Soc.*, 1953, **75**, 2486.
[3] T. Berzins and P. Delahay, *ibid.*, 1953, **75**, 4205.
[4] T. Kambara and I. Tachi, *J. Phys. Chem.*, 1957, **61**, 1405.
[5] Y. Takemori, T. Kambara, M. Senda and I. Tachi, *ibid.*, 1957, **61**, 968.
[6] C. Furlani and G. Morpurgo, *J. Electroanalyt. Chem.*, 1960, **1**, 351.
[7] A. C. Testa and W. H. Reinmuth, *Analyt. Chem.*, 1960, **32**, 1512.
[8] W. H. Reinmuth, *ibid.*, 1960, **32**, 1514.
[9] A. C. Testa and W. H. Reinmuth, *ibid.*, 1960, **32**, 1518.
[10] D. G. Peters and J. J. Lingane, *J. Electroanalyt. Chem.*, 1961, **2**, 1.
[11] *Idem, ibid.*, 1961, **2**, 249.
[12] T. O. Rouse, *PhD. Thesis*, University of Minnesota, Nov. 1960.
[13] W. H. Reinmuth, *Analyt. Chem.*, 1961, **33**, 322.
[14] A. C. Testa and W. H. Reinmuth, *ibid.*, 1961, **33**, 1324.
[15] R. M. King and C. N. Reilley, *J. Electroanalyt. Chem.*, 1960, **1**, 434.
[16] R. W. Murray and C. N. Reilley, *ibid.*, 1962, **3**, 64.
[17] *Idem, ibid.*, 1962, **3**, 182.
[18] P. Delahay, *Disc. Faraday Soc.*, 1954, **17**, 205.

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RADIOCHEMICAL DETERMINATION OF STRONTIUM-89 AND -90 IN URANIUM MINERALS AND SALTS

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Summary—A combination of low-level counting technique and large-scale analytical operation has been employed to determine extremely small quantities of strontium-89 and -90 in uranium ores and salts. Strontium carrier is added to a kilogram quantity of the samples of non-irradiated uranium ore and salt, exhaustively purified, and counted. The levels of radiostrontium found are of the order of 10^{-4} disintegrations.$sec^{-1}.g^{-1}$ of uranium in the sample. These strontium isotopes are formed in non-irradiated uranium salts and ores predominantly by the spontaneous fission of uranium, but neutron-induced fission of uranium-235 also appears to occur in the latter.

INTRODUCTION

THE existence of extremely small activities of natural fission-produced strontium-89 and -90 in pitchblende was first reported by Kuroda and Edwards[1] about a decade ago. Determination of these strontium isotopes in uranium ore is tedious and requires a large-scale chemical operation, which looks somewhat like a miniature version of Mme. Curie's experiment of the isolation of radium from pitchblende.

In connection with a study on the process of natural fission, currently being carried out in this laboratory, it was necessary to measure the levels of strontium-90 in pitchblende and in various uranium-bearing materials. The purpose of the experiment was to see if the amount of strontium-90 found in pitchblende agrees with the calculated amount from the known spontaneous fission half-life ($8{\cdot}0 \times 10^{15}$ years) of uranium-238, or if there is an excess of strontium-90 from the contribution by neutron-induced fission of uranium-235. The contribution from the latter process would imply that a nuclear chain reaction occurs in nature, *i.e.*, some of the neutrons produced by the uranium-238 spontaneous fission are absorbed by the uranium-235 atoms and produce additional fission neutrons.

The existence of such a nuclear chain-reacting system in nature has been demonstrated mass-spectrometrically.[2,3] The mass-spectrometric measurements deal, however, with the stable isotopes of krypton and xenon, and hence reveal the cumulative effects of the nuclear chain reaction throughout the life-time of the uranium ores.

Measurements of the levels of strontium-90 in pitchblende would tell us something about the extent to which the nuclear chain reaction is occurring "today" in the uranium ore. Knowing this, one may be able to compute the total number of uranium atoms which have participated in the nuclear chain reaction during the entire history of the earth.

The recent discovery that the earth's atmosphere appears to contain an excess of "fission-produced" xenon isotopes relative to the xenon extracted from meteorites can be explained from either (*a*) the contribution from the extinct transuranium element, such as plutonium-244 (half life: $7{\cdot}6 \times 10^7$ years),[4,5] or (*b*) the natural uranium chain reaction which occurred during the geological history of the earth.[6–9]

No attempt will be made in this paper to discuss fully the nuclear and geocosmochemical aspects of the process of natural fission. However, mention will be made here that pitchblende and other uranium ores are expected to contain similar activities of natural fission-produced technetium and promethium isotopes. These so-called "missing" elements can be also isolated from uranium ores by a large-scale chemical operation. Measurements of the levels of technetium and promethium activities in pitchblende are currently being continued in this laboratory.[10–15]

The present paper describes some of the analytical and radiochemical problems encountered in the separation and determination of the extremely small quantities of strontium-89 and -90 in kilogram-quantities of uranium ores. It has been our experience that the strontium fraction of pitchblende can be very easily lost during the chemical operation, even when a fairly large quantity of strontium carrier is added to the pitchblende sample. A failure in the recovery of the strontium fraction meant a loss of kilogram quantity of pitchblende, as well as a loss of "face" to the investigators involved in the operation. In fact, the experiment of Kuroda and Edwards[1] has never been successfully repeated in this laboratory and elsewhere until the new analytical scheme described in this paper was developed.

EXPERIMENTAL

Materials

A large quantity of African pitchblende and a sample of depleted uranium with the isotopic composition of 99·98% ^{238}U and 0·011% ^{235}U were made available to us for this study by Dr. H. M. Roth of the Research and Development Division, U.S. Atomic Energy Commission, Oak Ridge, Tennessee, U.S.A.

All reagents used in this work were of the highest purity obtainable, usually Reagent ACS purity.

Counting equipment

A CE14 Tracerlab Low-Background Beta Counter was used to count the strontium fractions isolated from pitchblende and depleted uranium.

Chemical procedure

A flow sheet of the chemical operations is shown in Fig. 1. The final adoption of the analytical scheme shown in Fig. 1. was based on the knowledge gained from the preliminary experiments on the behaviour of strontium as described in the latter part of this report.

In the case of the determination of radiostrontium in depleted uranium salt, the sample was converted to $UO_2(NO_3)_2{\cdot}6H_2O$, 200 mg of strontium carrier were added, and this was first treated with 80% nitric acid. The strontium nitrate found in the precipitate was then exhaustively purified and counted.

RESULTS AND DISCUSSION

The final strontium carbonate precipitate recovered from 2·6 kg of pitchblende weighed 124 mg and showed an activity of about 300 cpm. This activity was found to be mostly from the decay products of radium. The sample was dissolved in dilute nitric acid and was repurified, starting with the ion-exchange separation step of the flow sheet shown in Fig. 1.

The purified strontium carbonate precipitate weighed 114 mg and had a weak beta activity shown as Curve I in Fig. 2. The growth-decay curve observed indicated the presence of 50-day ^{89}Sr and the growth of 64·5-hour ^{90}Y from 28-year ^{90}Sr.

To calculate the radiostrontium content of the pitchblende, the chemical yield has

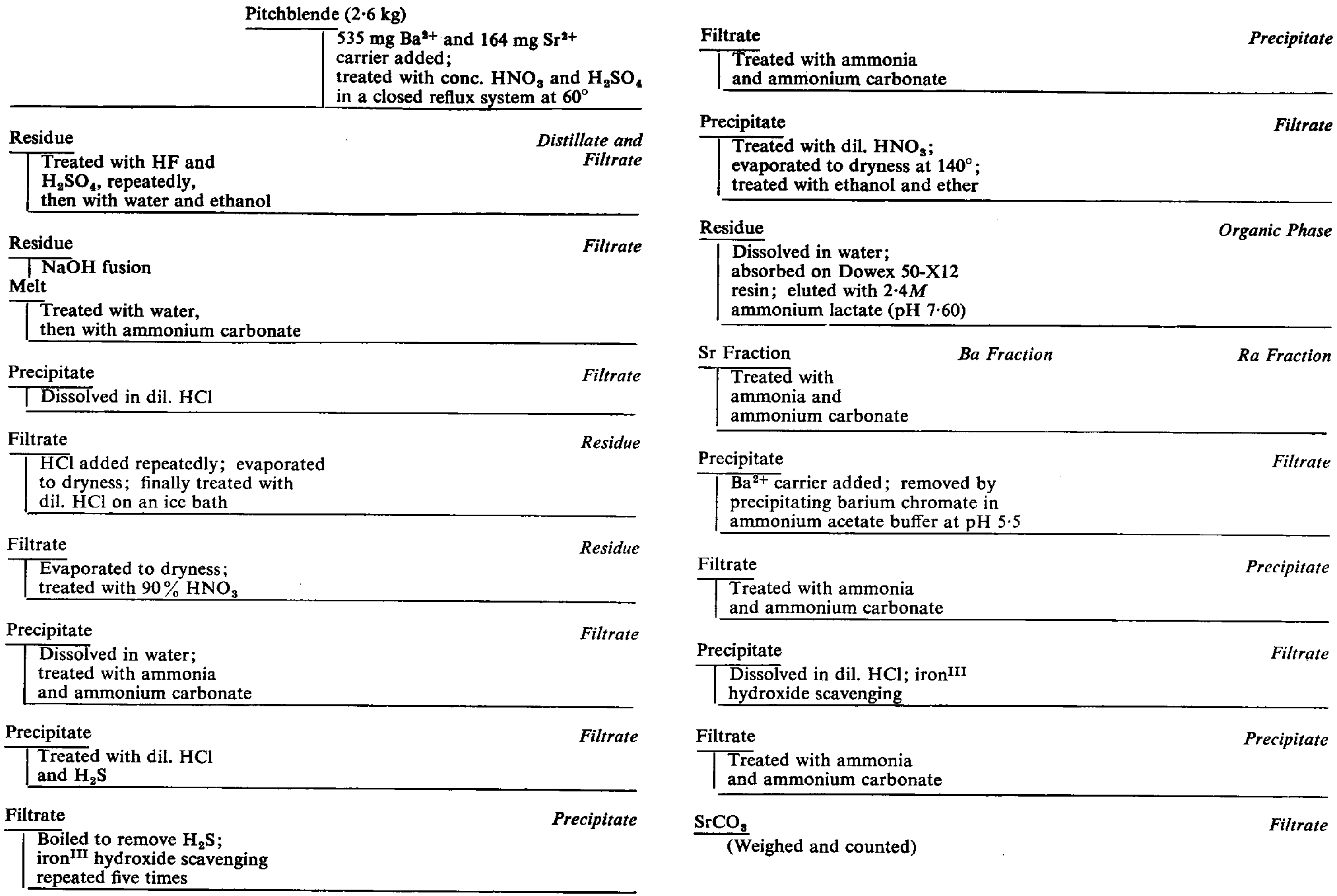

FIG. 1.—Flow diagram for the determination of strontium-90 in pitchblende.

to be accurately known. If a mg of strontium carrier were added and b mg were recovered, the chemical yield, y, is

$$y = \frac{b}{a + x} \cdot 100\% \tag{1}$$

where x is the amount of strontium originally present in the sample.

Attempts to determine x in the African pitchblende have all failed, and we are currently of the opinion that $x \ll a$. Thus, if one neglects x, the chemical yield in this case is calculated to be 42%, which is the highest chemical yield so far attained.

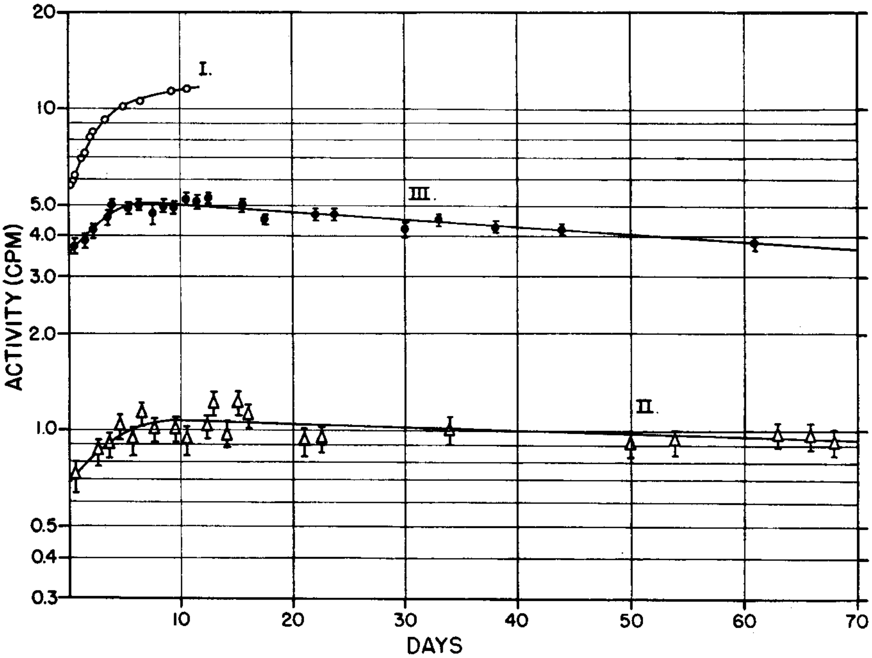

FIG. 2.—Radioactivity of the strontium fractions isolated from pitchblende and depleted uranium:

I—2,600 g of pitchblende; chemical yield: 42%;
II—3,750 g of pitchblende; chemical yield: 5%;
III—2,052 g of $^{238}UO_3$; chemical yield: 39%.

Numerous attempts made to recover strontium from acid-soluble fractions of the African pitchblende have all failed. The chemical yields were generally 5% or less in all such analytical schemes.

For example, strontium carrier (141 mg) was added to 3,750 g of the pitchblende, the whole being dissolved in dilute nitric acid; and, after the nitric acid was distilled off, the bulk of uranium was extracted with ether. The strontium carrier was recovered from the residue, after a lengthy chemical operation, with a chemical yield of only 5%. The counting data for the strontium fraction obtained in this experiment are shown in Fig. 2 as Curve II.

An attempt to separate the strontium fraction from 200 g of the pitchblende together with 150 mg of added barium carrier gave a chemical yield of only 3·7%. A chemical yield of 0% was obtained in many similar experiments.

All of these results suggest that the strontium is probably precipitated as the sulphate in the initial stage of the sample treatment, and hence it is almost impossible to recover the strontium fraction without the process of fusion.

The recovery of the strontium fraction from uranium salt is somewhat easier, in that the fusion step is not required. $^{238}UO_3$(2,052 g) was converted to

$$UO_2(NO_3)_2.6H_2O(2{,}945\ g)$$

and was treated with 40 litres of 80% nitric acid, after the addition of 200 mg of strontium carrier. The precipitate, which contained calcium, strontium, barium and radium, was converted to the carbonates. The carbonate precipitate was dissolved in dilute hydrochloric acid, and the iron^{III} hydroxide scavenging process was repeated three times. The purified carbonate precipitate was treated with nitric acid and evaporated to dryness. The strontium fraction was further purified according to an analytical scheme similar to that given in Fig. 1. The strontium was finally precipitated as the carbonate, filtered, dried and weighed. The chemical yield was 39%. The counting data are shown in Fig. 2 as Curve III.

TABLE I.—RADIOSTRONTIUM CONTENTS OF THE AFRICAN PITCHBLENDE AND DEPLETED URANIUM

Sample	Chemical yield, %	10^{-4} × Disintegrations. sec^{-1}. g^{-1} of uranium in the sample[b]	
		^{89}Sr	^{90}Sr
I. African pitchblende (2,600 g)[c]	42	3·5 ± 0·3	5·8 ± 0·5
II. African pitchblende (3,750 g)[d]	5·0	——[a]	3 ± 2
III. Depleted uranium (2,052 g) as $^{238}UO_3$[d]	39	2·8 ± 0·2	1·1 ± 0·1

[a] Measurement was impossible because about 200 days have elapsed since the initial separation of strontium from pitchblende.

[b] The errors reported here originate from uncertainty in analyzing the decay-growth curves.

[c] Sample I treated by fusion procedure.

[d] Samples II and III treated by acid-extraction procedure.

Precise determinations of the low-level activities of strontium-89 and -90 require at least a few months of careful counting, and hence only preliminary results can be reported here. Table I summarises the results obtained so far.

The results indicate that the strontium-89 and -90 are formed predominantly by the spontaneous fission of uranium-238. The equilibrium activity of the spontaneous fission-produced strontium-90 in uranium-bearing materials is calculated to be

$$\begin{aligned} N^{90}\lambda_{90} &= N^{238}\lambda_{238f} \,.\, Y^{90} \\ &= \frac{6{\cdot}02 \times 10^{23}}{238} \cdot \frac{\ln 2}{(8{\cdot}0 \times 10^{15})(3{\cdot}16 \times 10^{7})} \cdot (0{\cdot}05) \qquad (2) \\ &= 3{\cdot}5 \times 10^{-4}\ (\text{disintegrations. sec}^{-1}.\ \text{g}^{-1}\ \text{of uranium}), \end{aligned}$$

where N^{90} and N^{238} are the number of atoms of strontium-90 and uranium-238, respectively, λ_{90} is the decay constant of strontium-90, λ_{238f} is the spontaneous fission decay constant of uranium-238, and Y^{90} is the yield of mass 90 chain (tentatively assumed to be 5% in the above calculation).

The amount of strontium-90 in pitchblende appears to be considerably higher than the value calculated above, probably because of the contribution from the neutron-induced fission of uranium-235.

On the other hand, the level of strontium-90 in non-irradiated depleted uranium is much lower than that in uranium ore. This is most likely because the half-life of strontium-90 is greater than the "age" or the time elapsed since the preparation of the uranium salt. The results thus indicate that the secular equilibrium between strontium-90 and uranium is not yet established in the uranium salt. The following relationship should hold between the strontium-90/uranium-238 ratio and the "age" of the uranium salt:

$$N^{90}\lambda_{90} = N^{238}\lambda_{238f} \cdot Y^{90} \cdot (1 - e^{-\lambda_{90}t}) \tag{3}$$

where t is the "age" of the uranium salt. Thus it appears that the uranium salts can be dated from the observed strontium-90/uranium-238 ratios.

It is interesting to compare the activities of strontium-90 and radium in pitchblende. Because radium is expected to be also in secular equilibrium with uranium in pitchblende,

$$\frac{\text{Strontium-90 activity}}{\text{Radium-226 activity}} = \frac{\lambda_{238f}}{\lambda_{238\alpha}} \cdot Y^{90}, \tag{4}$$

where $\lambda_{238\alpha}$ is the alpha-decay constant of uranium-238.

Equation (4) yields a value of 28 mμc of strontium-90 per g of radium in pitchblende. This calculation shows that Mme. Curie must have handled quite a considerable activity of strontium-90 (in fact, roughly 60,000 disintegrations per min of strontium-90 per g of radium isolated from pitchblende!) during her experiments. This activity would have been well within the limit of detection of the electroscope used in those days. It is perhaps fortunate, though, that man did not discover the process of nuclear fission almost a half century earlier!

Acknowledgments—One of the authors (P.K.K.) would like to take this opportunity to thank his great teacher, Professor Kolthoff, not only for invaluable guidance, encouragement, advice and inspiration, but also for (i) allowing him to marry one of the pupils (Miss Loes Morren from the Hague, Netherlands), (ii) promptly giving a warm overcoat to the chemist just immigrated from Japan, who was shivering in the cold winter of Minnesota, and (iii) allowing him to consume a quite considerable quantity of his teacher's blood for the purely scientific purpose of developing a better method for the amperometric determination of -SH and -SS groups in biological samples, in connection with the cancer research project at the University of Minnesota.

This investigation was supported by the U.S. Atomic Energy Commission. We are grateful to Mr. J. C. Kizziar for his assistance.

Zusammenfassung—Durch Zählen bei niedrigen Zählraten und analytische Verarbeitung großer Mengen wurden extrem geringe Mengen von Strontium-89 und -90 in Uranerzen und -salzen bestimmt. Strontiumträger wurde zu Kilogramm-Mengen nicht bestrahlten Uranerzes bzw. -salzes gegeben, erschöpfend gereinigt und gezählt. Der Anteil von Radiostrontium lag in der Größenordnung von 10^{-4} Zerfällen pro Sekunde und Gramm U in der Probe. Diese Strontiumisotope werden in nicht bestrahlten Uransalzen und -erzen vorwiegend durch spontane Spaltung von Uran gebildet, in den Erzen scheint aber auch neutroneninduzierte Spaltung von Uran-235 vorzukommen.

Résumé—Une technique de comptage à bas niveau a été combinée à une opération analytique à grande échelle pour déterminer des quantités extrêmement faibles de strontium-89 et -90 contenues dans les minerais et les sels d'uranium. On a ajouté du strontium comme porteur à un échantillon d'un kilogramme de minerai et de sel d'uranium non irradié, parfaitement purifié et compté. Les niveaux du strontium radioactif étaient de l'ordre de 10^{-4} désintégration par seconde et par gramme d'uranium dans l'échantillon. Ces isotopes du strontium dans les sels et les minerais d'uranium non irradiés proviennent principalement de la fission naturelle de l'uranium, mais la fission induite par les neutrons de l'uranium-235 semble aussi se produire.

REFERENCES

[1] P. K. Kuroda and R. R. Edwards, *J. Chem. Phys.*, 1954, **22**, 1940.
[2] W. H. Fleming and H. G. Thode, *Phys. Rev.*, 1953, **92**, 378.
[3] G. W. Wetherill, *ibid.*, 1953, **92**, 907.
[4] P. K. Kuroda, *Nature*, 1960, **187**, 36.
[5] *Idem*, *Geochim. Cosmochim. Acta*, 1961, **24**, 40.
[6] *Idem*, *J. Chem. Phys.*, 1956, **25**, 781.
[7] *Idem*, *ibid.*, 1956, **25**, 1295.
[8] P. K. Kuroda, R. R. Edwards, B. L. Robinson, J. H. Jonte and C. Coolsby, *Geochim. Cosmochim. Acta*, 1957, **11**, 194.
[9] B. T. Kenna and P. K. Kuroda, *J. Inorg. Nuclear Chem.*, 1960, **16**, 1.
[10] *Idem*, *ibid.*, 1961, **23**, 142.
[11] B. T. Kenna, Ph.D. Dissertation, University of Arkansas, 1962.
[12] *Idem*, *J. Chem. Educ.*, 1962, **39**, 436.
[13] B. T. Kenna and P. K. Kuroda, *J. Inorg. Nuclear Chem.*, in press.
[14] M. P. Menon, Ph.D. Dissertation, University of Arkansas, 1963.
[15] M. P. Menon and P. K. Kuroda, *J. Inorg. Nuclear Chem.*, in press.

Talanta, 1964, Vol. 11, pp. 351 to 384. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS OF IZAAK MAURITS KOLTHOFF

1. Phosphoric acid as mono- and di-basic acid. *Chem. Weekblad*, 1915, **12,** 644–53.
2. Behaviour of phosphoric acid with calcium hydroxide. *Ibid.*, 1915, **12,** 662–6.
3. Volumetric determination of phosphoric acid in calcium phosphate. *Pharm. Weekblad*, 1915, **52,** 1053–5.
4. Examination of urine. *Ibid.*, 1916, **53,** 396–405.
5. Action of neutral salts on indicators. *Chem. Weekblad*, 1916, **13,** 284–97.
6. A chemical paradox. *Ibid.*, 1916, **13,** 1016–9.
7. Titration of hypophosphites. *Pharm. Weekblad*, 1916, **53,** 909–16.
8. Determination of alkalinity and phosphoric acid in the ash of foodstuffs. *Chem. Weekblad*, 1916, **13,** 910–4.
9. Reducing action of sugars. *Ibid.*, 1916, **13,** 887–95.
10. Detection of preservatives and colours in milk. *Pharm. Weekblad*, 1916, **53,** 1609–18.
11. The alcohol test in milk. *Ibid.*, 1916, **53,** 1589–600.
12. Qualitative analysis of carbohydrate mixtures. *Ibid.*, 1917, **54,** 205–14.
13. Accumulation of small amounts of heavy metals in drinking water. *Ibid.*, 1916, **53,** 1739–49.

14–16. Chemical study of potable waters: I. *Ibid.*, 1917, **54,** 547–53: II. *Ibid.*, **54,** 612–8: III. *Ibid.* **54,** 633–46.

17. Tin ash (With L. B. van Lohuizen). *Ibid.*, 1917, **54,** 718–20.
18. Argentometric determination of bromides and iodides. *Ibid.*, 1917, **54,** 761–6.
19. Determination of carbon dioxide and reactions of its various forms to indicators in potable waters. Active carbon dioxide. *Ibid.*, 1917, **54,** 982–92.
20. Determination of alkalinity and phosphoric acid in the ash of foods. *Chem. Weekblad*, 1917, **14,** 547–58.
21. Detection and determination of carbonate in bicarbonate. *Pharm. Weekblad*, 1917, **54,** 1046–51.

22–26. Study of potable waters: V–IX. *Ibid.*, 1917, **54,** 1005–20.

27. Titration of carbonic acid and its salts. *Chem. Weekblad*, 1917, **14,** 781–93.
28. Quantitative sugar determinations (With N. Schoorl). *Pharm. Weekblad*, 1917, **54,** 949–53.

29–30. Study of potable waters: X–XI. *Ibid.*, 1917, **54,** 1115–20.

31. Detection and determination of small amounts of hydrocyanic acid. *Ibid.*, 1917, **54,** 1157–71.
32. Chemical examination of stomach juices. *Ibid.*, 1917, **54,** 1192–200, 1253–8.
33. Unmixing in the system aniline-water-glycerol. *Chem. Weekblad*, 1917, **14,** 1081–9.
34. Preparation, properties and analysis of white precipitate. *Pharm. Weekblad*, 1918, **55,** 208–18.
35. Determination of water in glycerol. *Ibid.*, 1918, **55,** 304–7.

36. The dissociation constants of mercuric hydroxide. *Chem. Weekblad,* 1917, **14,** 1016–22.
37. The influence of neutral salts on the dissociation constants of indicators. *Ibid.* 1918, **15,** 394–400.
38. The titration of chlorides by Volhard's method. *Z. analyt. Chem.,* 1918, **56,** 568–77; *Chem. Weekblad,* 1918, **15,** 405.
39. The titration of chlorides by Volhard's method. *Pharm. Weekblad,* 1918, **55,** 1118–26.
40. Detection of acetone. *Ibid.,* 1918, **55,** 1021–9.
41. The importance of electrical conductivity in analytical chemistry. *Chem. Weekblad,* 1918, **15,** 889–96.
42. What are complex ions? *Ibid.,* 1917, **14,** 814–5.
43. Determination of glycerol by the method of Wagenaar (With J. H. M. Beckers). *Pharm. Weekblad,* 1918, **55,** 272–81.
44. Colour change and degree of dispersity of indicators (With H. R. Kruyt). *Kolloid-Z.,* 1917, **21,** 22–6.
45. Quantitative determination of sugar (With N. Schoorl). *Pharm. Weekblad,* 1918, **55,** 344–5 (1918).
46. Detection and determination of a small amount of hydrocyanic acid. *Z. analyt. Chem.,* 1918, **57,** 1–15.
47. The iodometric determination of copper. *Pharm. Weekblad,* 1918, **55,** 1338–46.
48. The determination of hypochlorites and chlorates in presence of each other. *Ibid.,* 1918, **55,** 1289–95.
49. The loss of hypochlorite content in standing solutions. *Ibid.,* 1918, **55,** 1318–24.
50. The importance of electrical conductivity in the analysis of potable waters. *Chem. Weekblad,* 1918, **15,** 1160–83.
51. Complex ions. *Ibid.,* 1918, **15,** 1636–44.
52. The use and evaluation of adsorbents. *Pharm. Weekblad,* 1919, **56,** 207–25, 237–58.

53–64. Iodometric studies. I. *Ibid.,* 1919, **56,** 391–3. II. *Ibid.,* 393–404. III. *Ibid.,* 426–38. IV. *Ibid.,* 460–5. V (With E. H. Vogelenzang). *Ibid.,* 514–24. VI. *Ibid.,* 572–85. VII. *Ibid.,* 621–34. VIII. *Ibid.,* 644–57. IX. *Ibid.,* 878–88. X. *Ibid.,* 949–59. XI. *Ibid.,* 1029–35. XII. *Ibid.,* 1298–300.

65. The detection of other alkaloids in quinine salts. *Ibid.,* 1919, **56,** 451–9.
66. Indicator test papers. *Ibid.,* 1919, **56,** 175–87.
67. The determination of sulphates as strontium sulphate (With E. H. Vogelenzang). *Z. analyt. Chem.,* 1919, **58,** 20–3.
68. The gravimetric determination of sulphate as barium sulphate (With E. H. Vogelenzang). *Pharm. Weekblad,* 1919, **56,** 122–42.
69. Estimation of copper by means of potassium thiocyanate, potassium iodide, thiosulphate. *Chem.-Ztg.,* 1919, **42,** 609–10.

70–76. Iodometric studies. XIII. *Pharm. Weekblad,* 1919, **56,** 1322–6. XIV. *Ibid.,* 1366–73. XV. *Ibid.,* 1413–20. XVI (With R. v. d. Heijde). *Ibid.,* 14 66–70. XVII (With R. v. d. Heijde). *Ibid.,* 1565–8. XVIII (With R. v. d. Heijde). *Ibid.,* 1618–26. XIX. *Ibid.,* 1920, **57,** 53–65.

77. The neutralisation curve of sulphurous acid. *Chem. Weekblad,* 1918, **16,** 1154–63.
78. The neutralisation curve of sulphurous acid. *Z. anorg. Chem.,* 1820, **109,** 69–79.

79. Indicators. *Pharm. Weekblad,* 1919, **56,** 404–6.
80. The oxidation potential of a ferri-ferrocyanide solution. *Chem. Weekblad,* 1919, **16,** 1406–15.
81. Oxidation potential of a ferri-ferrocyanide solution. *Z. anorg. Chem.,* 1920, **110,** 143–52.
82. Practical applications of iodometric titrations. *Chem. Weekblad,* 1920, **17,** 82–5.
83. Practical applications of iodometric titrations. *Ibid.,* 1920, **17,** 197–200.
84. The examination of salts for impurities giving an acid or alkaline reaction. *Pharm. Weekblad,* 1920, **57,** 252–65.
85. The determination of the composition of mixtures of alcohol and water by determination of the electrical conductivity. *Rec. Trav. chim.,* 1920, **39,** 126–34.
86. The titration of acid mixtures by the conductometric method. *Ibid.,* 1920, **39,** 280–302.
87. The third and fourth dissociation constants of pyrophosphoric acid and the purity tests for sodium pyrophosphate. *Pharm. Weekblad,* 1920, **57,** 474–81.
88. The titration of lead as lead chromate. *Ibid.,* 1920, **57,** 934–41.
89. The titration of potassium iodide with mercuric chloride. *Ibid.,* 1920, **57,** 836–42.
90. Neutralisation of weak acids by weak bases, and purity tests for ammonium salts of weak acids. *Ibid.,* 1920, **57,** 787–96.
91. The significance of dissociation constants in identifying acids and detecting impurities. *Ibid.,* 1920, **57,** 514–8.
92. The estimation of ferrous iron by electrometric titration. *Chem. Weekblad,* 1919, **16,** 450–61.
93. The oxidopotentiometric titration of iodides in the presence of chlorides and bromides. *Rec. Trav. chim.,* 1920, **39,** 208–4.
94–96. The application of electrometric titrations in neutralisation analysis. I. *Z. anorg. Chem.,* 1920, **111,** 1–28. II. *Ibid.,* 28–51. III. *Ibid.,* 97–108.
97. The separation of barium, strontium and calcium by the chromate method. *Pharm. Weekblad,* 1920, **57,** 1080–4.
98. The volumetric determination of barium and strontium as chromates. *Ibid.,* 1920, **57,** 927–9.
99. The iodometric determination of arsenic acid. *Ibid.,* 1921, **58,** 727–8.
100. Argentometric determination of iodides. *Ibid.,* 1921, **58,** 917–20.
101. The determination, calculation and significance of the hydrogen exponent in the analysis of potable waters. *Pharm. Weekblad,* 1921, **58,** 1005–20.
102. The electrometric titration of iodides by means of permanganate. *Rec. Trav. chim.,* 1921, **40,** 532–8.
103. The calculation and determination of the amount of active carbonic acid in drinking water. *Chem. Weekblad,* 1920, **17,** 390–6.
104. The content of active carbonic acid in drinking water. *Ibid.,* 1920, **17,** 558.
105. Calculation and determination of the content of active carbonic acid in potable water. *Z. Nahr. Genussm.,* 1921, **41,** 97–112.
106. Precipitation of the calcium group and of magnesium. *Pharm. Weekblad,* 1920, **57,** 1229–34.
107. Colorimetric determination of ammonia, nitrite and nitrate. *Ibid.,* 1920, **57,** 1253–64.

108–116. The significance of adsorption in analytical chemistry. I. *Ibid.*, 1920, **57,** 1510–5. II. *Ibid.*, 1515–29. III. *Ibid.*, 1571–7. IV. *Ibid.*, 1921, **58,** 46–56. V. *Ibid.*, 94–101. VI. *Ibid.*, 152–9. VII. *Ibid.*, 233–41. VIII. *Ibid.*, 401–7. IX. *Ibid.*, 463–71.

117. Review of the application of potentiometric titrations. *Chem. Weekblad,* 1920, **17,** 659–64.
118. The iodometric titration of chromic acid. *Z. analyt. Chem.*, 1920, **59,** 401–15.
119. End-point in oxidation titrations determined by means of the potentiometer. *Chem. Weekblad,* 1919, **16,** 408–16.
120. The determination of bases, combined with weak or moderately strong acids, and of very weak bases with acids and *vice versa. Z. anorg. Chem.*, 1921, **115,** 168–80.
121. The precipitation of tin by iron. *Rec. Trav. chim.*, 1920, **39,** 606–8.
122. The electrometric titration of phosphoric acid and its salts. *Z. anorg. Chem.*, 1920, **112,** 165–71.
123. The electrometric estimation of carbonic acid and its salts. *Ibid.*, 1920, **112,** 155–64.
124. The electrometric titrations of phenols. *Ibid.*, 1920, **112,** 187–95.
125. The electrometric titration of alkaloids and their salts. *Z. anorg. Chem.*, 1920, **112,** 196–208.
126. The acidimetric estimation of heavy metals in their salts. *Ibid.*, 1920, **112,** 172–86.
127. The indication of acid and basic function and their quantitative determination. *Rec. Trav. chim.*, 1920, **39,** 672–6.
128. Bromometric determination of salicyclic acid. *Pharm. Weekblad,* 1921, **58,** 699–702.
129. Estimation of the adsorbing power of charcoal. *Ibid.*, 1921, **58,** 630–56.
130. Estimation of the hydrogen exponent with colour indicator papers. *Ibid.*, 1921, **58,** 961–70.
131. The electrometric titration of iodides by means of permanganate. *Rec. Trav. chim.*, 1921, **40,** 532–8.
132. The application of the hydrogen electrode. *Chem. Weekblad,* 1921, **18,** 468–72.
133. Volumetric determination of zinc (With J. C. van Dijk). *Pharm. Weekblad,* 1921, **58,** 538–53.
134. Volumetric determination of ammonium salts with formalin. *Ibid.*, 1921, **58,** 1463–9.
135. Iodometric determination of iron. *Ibid.*, 1921, **58,** 1510–22.
136. The preparation of carbonate-free alkali. *Ibid.*, 1921, **58,** 1413–7.
137. The sensibility of indicator dyes at temperatures higher than ordinary temperatures. *Rec. Trav. chim.*, 1921, **40,** 775–85.
138. Determination of small amounts of bromides and chlorides in the presence of iodides. *Pharm. Weekblad,* 1921, **58,** 1568–9.
139. Separation of silver and mercury. *Ibid.*, 1921, **58,** 1680–3.
140. Detection of fructose in the presence of aldoses. *Chem. Weekblad,* 1922, **19,** 1–2.
141. Potassium ferricyanide as a standard in iodometry. *Pharm. Weekblad,* 1922, **59,** 66–8.

142. The acidimetric titration of dichromate (With E. H. Vogelenzang). *Rec. Trav. chim.*, 1921, **40,** 681–5.
143. The determination of sulphate by means of barium chromate suspensions. *Ibid.*, 1921, **40,** 686–9.
144. The salt error with coloring indicators. *Ibid.*, 1922, **41,** 54–67.
145. Argentometric titration of phosphoric acid. *Pharm. Weekblad*, 1922, **59,** 205–15.
146. Electroadsorption as a purely chemical phenomenon. *Kolloid-Z.*, 1922, **30,** 35–44.
147. Normal potential of silver. *Z. anorg. Chem.*, 1921, **119,** 202–12.
148. The sensibility of indicator dyes at temperatures higher than ordinary temperatures. *Rec. Trav. chim.*, 1921, **40,** 775–85.
149. Titration of moderately strong, in the presence of very weak, acids or bases. *Pharm. Weekblad*, 1922, **59,** 129–42.
150. Colorimetric determination of hydrogen-ion concentration without buffer. *Ibid.*, 1922, **59,** 104–18.
151. The use of the iodine electrode in potentiometric titrations. *Rec. Trav. chim.*, 1922, **41,** 172–91.
152. The hydrolysis of antipyrine salicylate. *Ibid.*, 1922, **41,** 135–44.
153. Application of conductometric titrations in analysis. *Chem. Weekblad*, 1920, **17,** 694–701.
154. Application of conductometric methods to precipitation analysis. *Z. analyt. Chem.*, 1922, **61,** 171–80.
155. The use of conductivity titrations in precipitation analysis. *Ibid.*, 1922, **61,** 229–40.
156. Conductivity titrations in precipitation analysis. *Ibid.*, 1922, **61,** 332–43.
157. The application of conductivity titrations in precipitation analysis. *Ibid.*, 1922, **61,** 369–77.
158. The use of potassium ferrocyanide in potentiometric titrations. *Rec. Trav. chim.*, 1922, **41,** 425–37.
159. Potentiometric titrations of potassium ferrocyanide and potentiometric titrations by means of ferrocyanide. *Ibid.*, 1922, **41,** 343–52.
160. Active carbonic acid and the hydrogen-ion concentration in water investigations. *Z. Nahr. Genussm.*, 1922, **43,** 184–92.
161. Qualitative reaction for arsenic. *Pharm. Weekblad*, 1922, **59,** 334–50.
162. Iodometric determination of arsenic acid. *Z. analyt. Chem.*, 1923, **62,** 137–8.
163. The use of conductivity titrations in precipitation analyses. *Ibid.*, 1922, **61,** 433–8.
164. Conductivity titration in precipitation analysis. *Ibid.*, 1923, **62,** 1–7.
165–168. The application of conductivity titrations in precipitation analysis. VIII. *Ibid.*, 1923, **62,** 161–78. IX. *Ibid.*, 209–14. X. *Ibid.*, 214–5. XI. *Ibid.*, 216–7.
169. Iodine determination in ferrous iodide pills. *Pharm. Weekblad*, 1922, **59,** 1100–3.
170. Detection of methanol in liquids containing ethyl alcohol. *Ibid.*, 1922, **59,** 1268–74.
171. Determination of chloral hydrate. *Ibid.*, 1923, **60,** 2–8.
172. Iodometric titration of sublimate. *Ibid.*, 1923, **60,** 18–20.
173. The determination of traces of invert sugar in sucrose. *Arch. Suikerind.*, 1922, **30,** 867–70.

174. The calculation of the salt content of drinking water from the electric conductivity. *Chem. Weekblad*, 1922, **19**, 407–9.
175. The successive titration of boric acid and phosphoric acid. *Ibid.*, 1922, **19**, 449–50.
176. Iodometric determination of antipyrine. *Pharm. Weekblad*, 1923, **60**, 194–9.
177. Colorimetric determinations of the water content of absolute alcohol. *Ibid.*, 1923, **60**, 227–31.
178. Titration of calcium hypochlorite. *Ibid.*, 1923, **60**, 241–8; *Rec. Trav. chim.*, 1922, **41**, 740–50.
179. The degree of acidity of milk. *Handel Genootsch. Melkk.*, 1920, **120**, Pt. 2, 5–16.
180. Acidimetric titration of magnesium in its salts. *Rec. Trav. chim.*, 1922, **41**, 787–94.
181. Iodometric determination of aldose. *Pharm. Weekblad*, 1923, **60**, 362–75.
182. The reaction between hypochlorite and potassium iodide. *Rec. Trav. chim.*, 1922, **41**, 615–26.
183. Adaptation of the iodometric aldose determination to the analysis of mixtures containing carbohydrate. *Pharm. Weekblad*, 1923, **60**, 394–402.
184. Compounds between sugars and salts. *Arch. Suikerind.*, 1923, **31**, 261–9.
185. Compounds between sugars and salts: II. *Ibid.*, 1923, **31**, 799–802.
186. Titration of iodides according to Winkler. *Pharm. Weekblad*, 1923, **60**, 841–5.
187. The influence of alcohol on the sensitiveness of dye indicators. *Rec. Trav. chim.*, 1923, **42**, 251–75.
188. The use of the quinhydrone electrode in place of the hydrogen electrode in potentiometric acidity determination. *Ibid.*, 1923, **42**, 186–98.
189. Colorimetric determination of hydrogen-ion concentration by the method of Michaelis with one-colour indicators, with inorganic solutions for colour comparison. *Pharm. Weekblad*, 1923, **60**, 949–66.
190. Estimation of the alkali metals as sulphates (With N. Schoorl). *Chem. Weekblad*, 1920, **17**, 425–7.
191. A new qualitative test for sodium. *Pharm. Weekblad*, 1923, **60**, 1251–5.
192. The detection and colorimetric determination of cyanide as thiocyanate. *Z. analyt. Chem.*, 1924, **63**, 188–90.
193. Influence of salts on the potential of the silver–silver bromide electrode. *Z. anorg. Chem.*, 1923, **132**, 117–24.
194. The adaptation of potassium permanganate to oxidimetry. *Pharm. Weekblad*, 1924, **61**, 133–7.
195. The dissociation constant of lithium hydroxide. The second dissociation constant of salicylic acid. *Rec. Trav. chim.*, 1923, **42**, 969–72.
196. The dissociation constants of the alkaline earth hydroxides. *Ibid.*, 1923, **42**, 973–9.
197. The salt error of nitramine (picrylmethylnitramine). *Ibid.*, 1923, **42**, 964–8.
198. The colorimetric determination of the hydrogen exponent of the soil. *Chem. Weekblad*, 1923, **20**, 675–7.
199. Spontaneous decomposition of permanganate under various conditions. *Pharm. Weekblad*, 1924, **61**, 337–43.
200. The use of diphenylcarbazide as a qualitative reagent on metals. *Chem. Weekblad*, 1924, **21**, 20–2.

201. The use of benzidine as reagent and also as indicator for a definite oxidation potential. *Ibid.*, 1924, **21,** 2–4.
202. The titration of oxalic acid with permanganate. *Pharm. Weekblad*, 1924, **61,** 377–90, 417–29.
203. The titration of oxalic acid with permanganate. *Z. analyt. Chem.*, 1924, **64,** 185–211.
204. The influence of some colloids on the titration of chlorine by the Volhard method. *Chem. Weekblad*, 1924, **21,** 188–9.
205. The use of mercury electrodes in potentiometric titrations. The determination of halogens, cyanides, sulphides and thiosulphate (With E. J. A. H. Verzijl). *Rec. Trav. chim.*, 1923, **42,** 1111.
206. Standardisation of permanganate with Mohr's salt. *Pharm. Weekblad*, 1924, **61,** 561–6.
207. The colorimetric determination of the hydrogen-ion concentration by the wedge method and the dissociation constants of various indicators. *Rec. Trav. chim.*, 1924, **43,** 144–52.
208. The second dissociation constant of sulphuric acid. *Rec. Trav. chim.*, 1924, **43,** 207–15.
209. The strength of the acid function of the sulphur-oxygen acids. *Ibid.*, 1924, **43,** 216–20.
210. Standardisation of permanganate with different reagents. *Pharm. Weekblad*, 1924, **61,** 786–9.
211. The titration of arsenious acid with permanganate. *Ibid.*, 1924, **61,** 738–42.
212. Volumetric analysis of hydrazine by the iodine, bromate, iodate and permanganate methods. *J. Amer. Chem. Soc.*, 1924, **46,** 2009–16.
213. Determination of sulphurous acid, thiosulphate and sulphide with potassium permanganate. *Pharm. Weekblad*, 1924, **61,** 841–6.
214. Oxidation of nitrous acid, hydrazine, ammonia and hypophosphite by permanganate. *Ibid.*, 1924, **61,** 954–60.
215. A double salt of ferricyanide of caesium and zinc (With E. J. A. H. Verzijl). *Rec. Trav. chim.*, 1924, **43,** 394–6.
216. The practical utility of the potentiometric titration of zinc with ferrocyanide (With E. J. A. H. Verzijl). *Ibid.*, 1924, **43,** 380–8.
217. The titration of zinc by means of different metallic ferrocyanides (With E. J. A. H. Verzijl). *Ibid.*, 1924, **43,** 389–93.
218. The standardisation of permanganate with various standard substances. *Z. analyt. Chem.*, 1924, **64,** 255–62.
219. The hydrostrychnine reagent for nitrites and nitrates. *Chem. Weekblad*, 1924, **21,** 423–4.
220. The titration of manganous salts with permanganate. *Pharm. Weekblad*, 1924, **61,** 1141–9.
221. The titration of ferrous salts with permanganate (With Nel Smit). *Ibid.*, 1924, **61,** 1082–95.
222. Determination of ammonium salts by acidimetric titration with formaldehyde. *Arch. Suikerind.*, 1924, **32,** 665–6.
223. The state of the silver in protargol and collargol. *Pharm. Weekblad*, 1924, **61,** 1280–5.

224. The application of titanous chloride to potentiometric titrations: I. *Rec. Trav. chim.*, 1924, **43,** 768–74.
225. The application of titanous chloride to potentiometric titrations: II (With O. Tomiček). *Ibid.*, 1924, **43,** 775–83.
226. The titration of ferric and cupric salts separately and in the presence of one another, also in the presence of antimony, by means of titanous chloride. *Rec. Trav. chim.*, 1924, **43,** 816–22.
227. A colour reaction for glycerol. *Pharm. Weekblad*, 1924, **61,** 1497–8.
228. Evaluation of morphine in opial. *Ibid.*, 1925, **62,** 106–8.
229. Evaluation of opial. *Ibid.*, 1925, **62,** 190–2.
230. A new set of buffer mixtures that can be prepared without the use of standardized acid or base. *J. Biol. Chem.*, 1925, **63,** 135–41.
231. The state of methyl red in the interval of its colour change. *Rec. Trav. chim.*, 1925, **44,** 75–81.
232. The state of methyl orange in the interval of its colour change. *Ibid.*, 1925, **44,** 68–74.
233. The adsorption of electrolytes on charcoal. *Proc. Acad. Sci. Amsterdam*, 1924, **27,** 742–9.
234. The use of bromophenol blue in the determination of alkaloids in galenical preparations and drugs. *Pharm. Weekblad*, 1925, **62,** 478–85.
235. The salt error of indicators in solutions poor in electrolytes. *Rec. Trav. chim.*, 1925, **44,** 275–8.
236. Detection and determination of *p*-saccharin in saccharin and crystallose. *Pharm. Weekblad*, 1925, **62,** 548–53.
237. The sensitive adaptation of the iodoform reaction and the detection of acetone in spirit. *Ibid.*, 1925, **62,** 652–5.
238. The reliability of the quinhydrone electrode for the measurement of hydrogen-ion concentration in various solutions. *Z. Physiol. Chem.*, 1925, **144,** 259–71.
239. The standard values for calculation of pH from measurements with hydrogen or quinhydrone electrode. *Chem. Weekblad*, 1925, **22,** 332–9.
240. Reactions in ionisation and catalysis. *Ibid.*, 1925, **22,** 356–7.
241. The titration of iodide with iodate. *Pharm. Weekblad*, 1925, **62,** 878–82.
242. Adaptation of the cyanogen iodide method to the titration of iodide and ferrous iron in syrup of ferrous iodide. *Ibid.*, 1925, **62,** 910–14.
243. The acid character of saccharin and related acids. The detection and determination of *p*-sulphamylbenzoic acid in saccharin and crystallose. *Rec. Trav. chim.*, 1925, **44,** 629–37.
244. Argentometric titration of iodide. *Pharm. Weekblad*, 1925, **62,** 1309–12.
245. The state of silver in protargol (argenti proteinatum) and collargol (colloid silver argentum crede). *J. Amer. Pharm. Assoc.*, 1925, **14,** 183–9.
246. The chemical state of protein solutions. *Chem. Weekblad*, 1925, **22,** 489–94.
247. The significance of pH in bacteriology. *Tijdschr. vergel. Geneeskunde*, 1925, **11,** 268–77.
248. Electrometric titration of alkaloids and the reaction of alkaloid salts. *Pharm. Weekblad*, 1925, **62,** 1287–93.
249. The reaction of neutral water and of distilled water. *Chem. Weekblad*, 1925, **22,** 590–4.

250. The interpretation of the neutralisation curves of mixtures of boric acid and polyhydric alcohols. *Rec. Trav. chim.*, 1925, **44,** 975–82.
251. The reaction of neutral and distilled water. *Biochem. Z.*, 1926, **168,** 110–21.
252. Standardisation of hydrochloric acid against potassium iodate compared with results obtained against soda and borax. *Pharm. Weekblad*, 1926, **63,** 37–48.
253. A simple method for determination of nitrobenzene. *Chem. Weekblad*, 1925, **22,** 558–9.
254. Standardisation of hydrochloric acid with potassium iodate as compared with borax and sodium carbonate as standard substances. *J. Amer. Chem. Soc.*, 1926, **48,** 1447–54.
255. A modification of Schoorl's titration of sugars. *Chem. Weekblad*, 1926, **23,** 61–2.
256. Clarification of urine containing sugar with charcoal. *Biochem. Z.*, 1926, **168,** 122–7.
257. The reaction between cupric copper and iodide and between cuprous iodide and iodine. *Rec. Trav. chim.*, 1926, **45,** 152–61.
258. The iodometric determination of cuprous oxide in sugar titrations. *Arch. Suikerind.*, 1926, **34,** 123–30.
259. Note on the significance of the reaction in refinery operation. *Ibid.*, 1926, **34,** 130–4.
260. The dissociation constants, solubility product and titration of alkaloids. *Biochem. Z.*, 1925, **162,** 289–353.
261. Detection and determination of free chlorine in drinking water. *Chem. Weekblad*, 1926, **23,** 203–4.
262. The hydration of dissolved sucrose and the expression of the concentration by measuring the activity of the ions. *Verslag. Akad. Wetenschappen Amsterdam*, 1926, **35,** 281–95.
263. The methyl orange error in the colorimetric pH determination by comparison with Clark's buffer mixtures. *Rec. Trav. chim.*, 1926, **45,** 433–5.
264. The influence of boric acid on the electrolytic dissociation of electrolytes. *Ibid.*, 1926, **45,** 394–9.
265. The change of the dissociation constant of boric acid with the concentration of this acid. *Ibid.*, 1926, **45,** 501–7.
266. The expression of the reaction of aqueous solutions. *Biochem. Z.*, 1926, **169,** 490–3.
267. The carbon-dioxide content of distilled water and its determination. *Chem. Weekblad*, 1926, **23,** 381–4.
268. The microtitration of iodides with iodate and the determination of the iodide and ferrous iron content in syrup of ferrous iodide. *J. Amer. Pharm. Assoc.*, 1926, **15,** 164–6.
269. The titration of hypophosphorous acid and hypophosphites with permanganate. *Z. analyt. Chem.*, 1926, **69,** 36–8.
270. Hydration of dissolved sucrose and the expression of the concentration in measuring the activity of ions. *Proc. Acad. Sci. Amsterdam*, 1926, **29,** 885–98.
271. The Dénigès reaction for citric acid. *Pharm. Weekblad*, 1926, **63,** 1322–3.
272. Influence of chlorides on the Dénigès reaction for citric acid. *Ibid.*, 1926, **63,** 1453–5.

273. The carbon dioxide content of distilled water and its exact determination. *Biochem. Z.*, 1926, **176**, 101–9.
274. Reduction-oxidation potentials. A comment on the paper by P. Hirsch and R. Rüter. *Z. analyt. Chem.*, 1926, **69**, 374–7.
275. Iodometric titration of acids. *Chem. Weekblad*, 1926, **23**, 260–1.
276. Micro-titration of iodide. *Mikrochemie*, 1925, **3**, 75–9.
277. Complex-dissociation constants of compounds of boric acid with salts of some organic hydroxyacids. *Rec. Trav. chim.*, 1926, **45**, 607–19.
278. The volatility of borax. *Nature*, 1927, **119**, 425–6.
279. The argentometric determination of iodide in the presence of chloride with adsorption indicators as recommended by Fajans. *Z. analyt. Chem.*, 1927, **70**, 395–7.
280. A specific reagent for sodium ions. *Ibid.*, 1927, **70**, 397–400.
281. The titration of hydroquinone with iodine or dichromate according to the ordinary and the potentiometric method. *Rec. Trav. chim.*, 1926, **43**, 743–52.
282. The use of methoxytriphenylcarbinols as one-color indicators. *J. Amer. Chem. Soc.*, 1927, **49**, 1218–21.
283. The direct titration of zinc with potassium ferrocyanide with diphenylamine or diphenylbenzidine as indicators. *Chem. Weekblad*, 1927, **24**, 203–4.
284. The argentometric titration of chloride and iodide with adsorption indicators. *Z. analyt. Chem.*, 1927, **71**, 235–43.
285. A new specific colour test and a colorimetric method for determining traces of magnesium. *Chem. Weekblad*, 1927, **24**, 254–5.
286. A new specific colour reaction of magnesium and a simple colorimetric method for the determination of traces of this element. *Biochem. Z.*, 1927, **185**, 344–8.
287. The dissociation constant of hypophosphorous acid, phosphorous acid and phosphoric acid. *Rec. Trav. chim.*, 1927, **46**, 350–8.
288. A determination of the basic constant of morphine and its application in the titration of morphine. *Pharm. J.*, 1927, **118**, 126–7.
289. The use of potassium bi-iodate as a standard substance in alkalimetric and iodometric titrations (With L. H. Van Berk). *J. Amer. Chem. Soc.*, 1926, **48**, 2799–801.
290. The accuracy of halide and thiocyanate titration according to Fajans and according to the usual methods compared to the results of potentiometric determinations (With L. H. Van Berk). *Z. analyt. Chem.*, 1927, **70**, 369–94.
291. The use of yellow mercuric oxide and of metallic mercury as standards in volumetric analysis (With L. H. Van Berk). *Ibid.*, 1927, **71**, 339–49.
292. The application of the quinhydrone electrode to solutions with a low buffer capacity (With Wouter Bosch). *Chem. Weekblad*, 1927, **24**, 78–80.
293. A correction for the new citrate buffers (With J. J. Vleeschhouwer). *Ibid.*, 1927, **24**, 78.
294. The abnormal change in pH in boric acid-sodium hydroxide mixtures at different concentrations and temperatures (With Wouter Bosch). *Rec. Trav. chim.*, 1927, **46**, 180–8.
295. The use of the quinhydrone electrode for measuring the hydrogen-ion concentration in solutions of low buffer capacity (With Wouter Bosch). *Biochem. Z.*, **183**, 434–43.

296. The influence of neutral salts on acid-salt equilibria: I. (With Wouter Bosch). *Rec. Trav. chim.*, 1927, **46,** 430–8.
297. The potentiometric determination of the hydrogen ion concentration at higher temperatures (With F. Tekelenburg). *Proc. Acad. Sci. Amsterdam*, 1926, **29,** 766–75.
298. The change of the pH in buffer mixtures at varying temperatures (With F. Tekelenburg). *Rec. Trav. chim.*, 1927, **46,** 33–41.
299. The potentiometric determination of ferrous and ferrocyanide ions with potassium bromate (With J. J. Vleeschhouwer). *Ibid.*, 1926, **45,** 923–7.
300. A new set of buffer mixtures of pH 2·2 to 6·0 (With J. J. Vleeschhouwer). *Chem. Weekblad*, 1926, **23,** 510.
301. A new series of buffer solutions of a pH range between 2·2 and 6·0 (With J. J. Vleeschhouwer). *Biochem. Z.*, 1926, **179,** 410–3.
302. A correction to the new buffer solution series (With J. J. Vleeschhouwer). *Ibid.*, 1927, **183,** 444–5.
303. Displacement of chemical equilibria at an interface. *Kolloid-Z.*, 1927, **43,** 51.
304. A sensitive reaction of aluminium: the colorimetric determination of this element. *Chem. Weekblad*, 1927, **24,** 447–8.
305. Adsorption of electrolytes on pure ash-free carbon. *Rec. Trav. chim.*, 1927, **46,** 549–73.
306. The adsorption of strong electrolytes on pure ash-free charcoal. *Z. Elektrochem. angew. physik. Chem.*, 1927, **23,** 497–501.
307. The use of mixed indicators in acidimetry or alkalimetry. *Biochem. Z.*, 1927, **189,** 26–32.
308. The detection and determination of metals by means of 8-hydroxyquinoline (oxine). *Chem. Weekblad*, 1927, **24,** 606–10.
309. The detection of traces of beryllium and the colorimetric determinations of this element. *J. Amer. Chem. Soc.*, 1928, **50,** 393–5.
310. The exact determination of the equivalence point in potentiometric titrations. *Rec. Trav. chim.*, 1928, **47,** 397–400.
311. Colloidal silver preparation. *Pharm. Weekblad*, 1928, **65,** 362–5.
312. The use of quinaldine red for hydrogen-ion concentration determinations in acid medium. *Biochem. Z.*, 1928, **194,** 78–82.
313. The use of pinachrome as a one-color indicator. *J. Amer. Chem. Soc.*, 1928, **50,** 1604–8.
314. The determination and colorimetric determination of traces of aluminum. *J. Amer. Pharm. Assoc.*, 1928, **17,** 360–1.
315. Rapid method for the separation of aluminum and beryllium (With Ernest B. Sandell). *J. Amer. Chem. Soc.*, 1928, **50,** 1900–4.
316. The dissociation constant of naphthylaminesulphonic acid. *Chem. Weekblad*, 1928, **25,** 234.
317. Effect of dilution on the pH of buffer mixtures. *Biochem. Z.*, 1928, **195,** 239–47.

318–320. The influence of neutral salts on acid-salt equilibria (With Wouter Bosch): II. *Rec. Trav. chim.*, 1928, **47,** 558–75. III. *Ibid.*, 819–25. IV. *Ibid.*, 826–33.

321. Volumetric determination of ammonia with hypobromite according to the usual method and by the potentiometric method (With A. Laur). *Z. analyt. Chem.*, 1928, **73,** 196–200.

322. Gravimetric determination of copper as thiocyanate (With G. H. P. v. d. Meene). *Ibid.*, 1927, **72,** 337–45.
323. The completion of the series of buffer mixtures for the alkaline range (With J. J. Vleeschhouwer). *Biochem. Z.*, 1927, **189,** 191–3.
324. Addition to the series of buffer solutions in the alkaline range (With J. J. Vleeschhouwer). *Chem. Weekblad*, 1927, **24,** 526.
325. A specific reagent for the rapid gravimetric determination of sodium (With H. H. Barber). *J. Amer. Chem. Soc.*, 1928, **50,** 1625–31.
326. The salt error of indicators in the colorimetric determination of pH. *J. Phys. Chem.*, 1928, **32,** 1820–33.
327. Directions for the preparation of a "universal indicator" for estimating pH over a wide range. *Pharm. Weekblad*, 1929, **66,** 67–70.
328. Influence of sucrose on the dissociation constant of weak acids in aqueous solution. *Rec. Trav. chim.*, 1929, **48,** 220–6.
329. The decomposition of aqueous bromide and of bromic acid solution by charcoal. *Ibid.*, 1929, **48,** 291–7.
330. The influence of charcoal upon the velocity of the reaction between iodide-iodate and hydrogen ions, the decomposition of thiosulphuric acid and the reaction between phenol and bromine. *Ibid.*, 1929, **48,** 298–309.
331. Zinc uranyl acetate as a reagent for sodium. *Chem. Weekblad*, 1929, **26,** 294–8.
332. Titration of potassium ferrocyanide with diphenylamine as internal indicator. *Ibid.*, 1929, **26,** 298–301.
333. The "water correction" in the measurement of the electrical conductivity of very dilute aqueous solutions of electrolytes. *Rec. Trav. chim.*, 1929, **48,** 664–80.
334–336. The influence of neutral salts on acid-base equilibria (With W. Bosch): V. *Rec. Trav. chim.*, 1928, **47,** 861–72. VI. *Ibid.*, 872–82. VII. *Ibid.*, 1929, **48,** 1929, 37–48.
337. The adsorption of hydroxybenzenes and other aromatic compounds and their displacement of each other at the interface water-charcoal (With Els van der Goot). *Rec. Trav. chim.*, 1929, **48,** 265–87.
338. Measurement of the hydrogen-ion concentration in unbuffered solutions: I (With Tohru Kameda). *J. Amer. Chem. Soc.*, 1929, **51,** 2888–2900.
339. Volumetric determination of manganese as dioxide with special reference to the application of potassium bromate as oxidizing agent (With Ernest B. Sandell). *Ind. Eng. Chem., Analyt.*, 1929, **1,** 181–5.
340. Lecture demonstrations in analytical chemistry. *J. Chem. Educ.* 1929, **6,** 1910–5.
341. Confusion in the expression of the so-called "hydrogen-ion concentration" of a solution and a review of Brønsted's conception of acidity and basicity. *Rec. Trav. chim.*, 1930, **49,** 401–14.
342. Two delicate tests for the detection of copper with some remarks on the rhodanine test of Feigl for silver. *J. Amer. Chem. Soc.*, 1930, **52,** 2222–6.
343. Conductometric titration. *Ind. Eng. Chem., Analyt.*, 1930, **2,** 225–30.
344. Indicator constants. *J. Phys. Chem.*, 1930, **34,** 1466–83.
345. The cobalt thiocyanate reaction for the detection of cobalt and thiocyanate. *Microchemie* (*N.S.*), 1930, **2,** 176–81.

346. Ionic activity products and ionic activity constants. *Chem. Weekblad*, 1930, **27**, 250–61.
347. Use of dichlorofluorescein as an adsorption indicator for the argentometric titration of chlorides (With W. M. Lauer and C. J. Sunde). *J. Amer. Chem. Soc.*, 1929, **51**, 3273–7.
348. Determination of chromium and vanadium after oxidation with potassium bromate. Separate titration of chromate and vanadate in the same solution and application of the method to steel analysis (With Ernest B. Sandell). *Ind. Eng. Chem., Analyt.*, 1930, **2**, 140–5.
349. Properties of diphenylamine and diphenylbenzidine as reduction-oxidation indicators (With L. A. Sarver). *Z. Elektrochem.*, 1930, **36**, 139–41.
350. Gravimetric determination of sodium by the uranyl zinc acetate method. II (With H. H. Barber). *J. Amer. Chem. Soc.*, 1929, **51**, 3233–7.
351. The "drop method" apparatus of Todt for the colorimetric determination of pH values. *Chem. Weekblad*, 1931, **28**, 78–9.
352. The "drop method" apparatus of Todt for the colorimetric determination of pH. *Ibid.*, 1931, **28**, 262.
353. Acid-base-catalysis according to J. N. Brønsted. *Ibid.*, 1930, **28**, 110–21.
354. Color reactions for magnesium. *Mikrochem., Emich Festschr.*, 1930, 180–90.
355. The dissociation of acid-base indicators in ethyl alcohol with a discussion of the medium effect upon the indicator properties. *J. Phys. Chem.*, 1931, **35**, 2732–48.
356. The sensitivity of chemical precipitations. *Z. analyt. Chem.*, 1931, **86**, 34–40.
357. Lanthanum alkali oxalates (With Ruth Elmquist). *J. Amer. Chem. Soc.*, 1931, **53**, 1232–6.
358. The solubilities of lanthanum oxalate and of lanthanum hydroxide in water. The mobility of the lanthanum ion at 25° (With Ruth Elmquist). *Ibid.*, 1931, **53**, 1217–25.
359. The quantitative determination of lanthanum by precipitation as oxalate or as hydroxide and the higher oxide formation of lanthanum (With Ruth Elmquist). *Ibid.*, 1931, **53**, 1225–32.
360. The measurement of the hydrogen-ion concentration in unbuffered solutions: II (With Tohru Kameda). *Ibid.*, 1931, **53**, 821–4.
361. Conductometric titration of sulfate and barium (With Tohru Kameda). *Ind. Eng. Chem., Analyt.*, 1931, **3**, 129–33.
362. The hydrolysis of zinc sulfate solutions, solubility product of hydrous zinc oxide and the composition of the latter precipitated from zinc sulfate solutions (With Tohru Kameda). *J. Amer. Chem. Soc.*, 1931, **53**, 832–42.
363. Stability of potassium ferrocyanide solutions (With E. A. Pearson). *Ind. Eng. Chem., Analyt.*, 1931, **3**, 381–2.
364. Direct and reverse titration of sulfuric acid with barium hydroxide (With E. B. Sandell). *Ibid.*, 1931, **3**, 115–7.
365. Properties of diphenylamine and diphenylbenzidine as oxidation-reduction indicators (With L. A. Sarver). *J. Amer. Chem. Soc.*, 1930, **52**, 4179–91.
366. The reaction between nitrite and iodide and its application to the iodimetric titration of these anions (With Carlos A. Abeledo). *Ibid.*, 1931, **53**, 2893–7.
367. Diphenylaminesulfonic acid as a new oxidation-reduction indicator (With L. A. Sarver). *Ibid.*, 1931, **53**, 2902–5.

368. Indicator corrections for diphenylamine, diphenylbenzidine and diphenylaminesulfonic acid (With L. A. Sarver). *Ibid.*, 1931, **53**, 2906–9.
369. Solubilities and solubility products of metallic sulfides in water. *J. Phys. Chem.*, 1931, **35**, 2711–21.
370. The theory of coprecipitation-formation and properties of crystalline precipitates. *Ibid.*, 1932, **36**, 860–81.
371–374. Formation and properties of precipitates. Theory of coprecipitation: IV. *Chem. Weekblad.*, 1932, **29**, 346–8. V. *Ibid.*, 362–3. VI. *Ibid.*, 378–80. VII. *Ibid.*, 395–400.
375. Formation and properties of precipitates, theory of coprecipitation. *Ibid.*, 1932, **29**, 442–8.
376. The activity coefficient of benzoic acid in solutions of neutral salts and of sodium benzoate (With Wouter Bosch). *J. Phys. Chem.*, 1932, **36**, 1685–94.
377. The ionization constant of benzoic acid and the activity coefficient of benzoate ion in presence of neutral salts (With Wouter Bosch). *Ibid.*, 1932, **36**, 1695–1701.
378. The mean and individual ion activity coefficients of silver benzoate in salt solutions (With Wouter Bosch). *Ibid.*, 1932, **36**, 1702–11.
379. Titration of zinc with potassium ferrocyanide. Use of diphenylamine or diphenylbenzidine as internal indicators (With E. A. Pearson). *Ind. Eng. Chem., Analyt.*, 1932, **4**, 147–50.
380. Composition of precipitated copper sulfide (With E. A. Pearson). *J. Phys. Chem.*, 1932, **36**, 642–5.
381. The promoting action of copper sulfide on the speed of precipitation of zinc sulfide. The so-called coprecipitation of zinc with copper sulfide (With E. A. Pearson). *Ibid.*, 1932, **36**, 549–66.
382. The adsorption of cations from ammoniacal solution of silica gel (With V. A. Stenger). *Ibid.*, **36**, 2113–26.
383. The analytical adaptation of bromine substitution in phenols. *Pharm. Weekblad*, 1932, **69**, 1147–58.
384. Bromine substitution in salicylic acid. *Ibid.*, 1932, **69**, 1159–61.
385. Properties of active charcoal reactivated in oxygen at 400°. *J. Amer. Chem. Soc.*, 1932, **54**, 4473–80.
386. Volumetric determination of uranium with potassium dichromate as reagent and the application of the method to the indirect titration of minute quantities of sodium (With J. J. Lingane). *Ibid.*, 1933, **55**, 1871–6.
387. Diphenylaminesulfonic acid as a reagent for the colorimetric determination of nitrates. (With G. E. Noponen). *Ibid.*, 1933, **55**, 1448–53.
388. Specific surface and the adsorbent properties of lead sulfate (With Charles Rosenblum). *Ibid.*, 1933, **55**, 851.
389. The adsorbent properties and the specific surface of lead sulfate (With Charles Rosenblum). *Ibid.*, 1933, **55**, 2656–64.
390. The adsorption of Ponceau 4R (New Coccine) and methylene blue by lead sulfate and the effect of adsorbed Ponceau on the speed of kinetic exchange (With Charles Rosenblum). *J. Amer. Chem. Soc.*, 1933, **55**, 2664–72.
391. Exchange adsorption and its influence upon the solubility of precipitates with ionic lattices in electrolytic solutions (With E. B. Sandell). *Ibid.*, 1933, **55**, 2170–1.

392–394. Coprecipitation (With E. B. Sandell): IV. *J. Phys. Chem.*, 1933, **37,** 443–58. V. *Ibid.*, 459–73. VI. *Ibid.*, 723–33.

395. Nephelometric determination of chloride (With Henry Yutzy). *J. Amer. Chem. Soc.*, 1933, **55,** 1915–22.

396. Studies in coprecipitation: III (With E. B. Sandell). *J. Phys. Chem.*, 1933, **37,** 153–70.

397. The formation and properties of precipitates. Theory of coprecipitation. *Chem. Weekblad*, 1934, **31,** 102–3.

398–399. Theory of coprecipitation: IIA. *Ibid.*, 1934, **31,** 230–7. IIB. *Ibid.*, 244–51.

400. Gravimetric and volumetric determination of antipyrine in the presence of amidopyrine. *J. Amer. Pharm. Assoc.*, 1933, **22,** 947–50.

401. Exchange adsorption and adsorption indicators. *Kolloid-Z.*, 1934, **68,** 190–200.

402. Titration of chloride and bromide with mercurous nitrate using bromophenol blue as adsorption indicator (With W. D. Larson). *J. Amer. Chem. Soc.*, 1934, **56,** 1881–4.

403. The gravimetric and volumetric determination of brucine and strychnine as dichromate (With J. J. Lingane). *J. Amer. Pharm. Assoc.*, 1934, **23,** 404–8.

404. The free mobility of lead ions in amicronic crystals of lead sulfate (With Charles Rosenblum). *Phys. Rev.*, 1934, **45,** 341.

405–406. Structural changes taking place during the aging of freshly formed precipitates (With Charles Rosenblum): I. *J. Amer. Chem. Soc.*, 1934, **56,** 1264–9. II. *Ibid.*, 1658–61.

407. Detection and estimation of small amounts of fluorine. Application of the zirconium-purpurin test (With Maurice E. Stansby). *Ind. Eng. Chem., Analyt.* 1934, **6,** 118–21.

408–409. Adsorption from ammoniacal solution (With V. A. Stenger): II. *J. Phys. Chem.*, 1934, **38,** 249–58. III. *Ibid.*, 475–86.

410. The solubilities of calcium hydroxide, calcium iodate and ammonium perchlorate in dilute ammoniacal solutions (With V. A. Stenger). *J. Phys. Chem.*, 1934, **38,** 639–43.

411. The benzoate method. A new procedure for the separation of iron, aluminum and chromium from the other ions of the third group and the alkaline earth ions (With V. A. Stenger and B. Moskovitz). *J. Amer. Chem. Soc.*, 1934, **56,** 812–15.

412. The adsorption of wool violet (4BN) by lead sulfate and the effect of the adsorbed dye on the speed of kinetic exchange (With W. von Fischer and Charles Rosenblum). *Ibid.*, 1934, **56,** 832–6.

413. The dissociation of some inorganic acids, bases and salts in glacial acetic acid as solvent (With A. Willman). *Ibid.*, 1934, **56,** 1007–13.

414. The acid strength of inorganic cations and the basic strength of inorganic acetates in acetic acid: II (With A. Willman). *Ibid.*, 1934, **56,** 1014–16.

415. Chronometric catalytic method for the determination of micro quantities of iodine (With E. B. Sandell). *Ibid.*, 1934, **56,** 1426.

416. Reply to N. A. Brunt. *Chem. Weekblad*, 1935, **32,** 448–9.

417. Coprecipitation and postprecipitation. Aging of precipitates. *Z. analyt. Chem.*, 1936, **104,** 321–33.

418. Indicators. *Ind. Eng. Chem., Analyt.*, 1936, **8,** 237–9.

419. The adsorption of electrolytes on crystal surfaces. Reply to L. de Brouckers. *Chem. Weekblad*, 1936, **33**, 321–4.
420. The adsorbant properties of barium sulphate. *Bull. Soc. chim. belges*, 1936, **45**, 270–8.
421. Potassium thiocyanate as a primary standard substance (With J. J. Lingane). *J. Amer. Chem. Soc.*, 1935, **57**, 2126–31.
422. Accuracy of the titration of thiocyanate with mercuric mercury (With J. J. Lingane). *Ibid.*, 1935, **57**, 2377–9.
423. The accuracy of the potentiometric iodide-silver titration (With J. J. Lingane). *Ibid.*, 1936, **58**, 1524–8.
424. Absorption of silver and iodide ions by freshly precipitated silver iodide-isoelectric point of the fresh precipitate (With J. J. Lingane). *Ibid.*, 1936, **58**, 1528–33.
425–426. Structural changes taking place during aging of precipitates (With W. M. MacNevin): IX. *J. Amer. Chem. Soc.*, 1936, **58**, 499–504. X. *Ibid.*, 725–8.
427. Adsorption of barium salts on barium sulfate from solutions in 50% ethanol (With Wm. M. MacNevin). *Ibid.*, 1936, **58**, 1543–6.
428. Induced precipitations and properties of metal sulfides (With D. R. Moltzau). *Chem. Rev.*, 1935, **17**, 293–325.
429. Postprecipitation of zinc sulfide with mercuric sulfide (With D. R. Moltzau). *J. Phys. Chem.*, 1936, **40**, 779–98.
430. The constitution of β-iron oxide monohydrate (With B. Moskovitz). *J. Amer. Chem. Soc.*, 1936, **58**, 777–9.
431–434. Structural changes taking place upon aging of freshly prepared crystalline precipitates (With Charles Rosenblum): V. *Ibid.*, 1935, **57**, 2573–7. VI. *Ibid.*, 2577–9. VII. *Ibid.*, 1936, **58**, 116–20. VIII. *Ibid.*, 121–2.
435. The fourth ionization constant of ferrocyanic acid (With Wm. J. Tomsicek). *J. Phys. Chem.*, 1935, **39**, 955–8.
436. The oxidation potential of the system potassium ferrocyanide/potassium ferricyanide at various ionic strengths (With Wm. J. Tomsicek). *Ibid.*, 1935, **39**, 945–54.
437. Oxidation potential of the system potassium molybdocyanide/potassium molybdicyanide, and the effect of neutral salts on the potential (With Wm. J. Tomsicek). *Ibid.*, 1936, **40**, 247–55.
438. Mixed crystal formation of zinc sulfide postprecipitated with mercuric sulfide. The aging of mercuric sulfide and of zinc sulfide (With R. Moltzau). *Ibid.*, 1936, **40**, 637–43.
439. Modified persulfate-arsenite method for manganese with special reference to steel analysis (With E. B. Sandell and J. J. Lingane). *Ind. Eng. Chem., Analyt.*, 1935, **7**, 256–8.
440. Detection and colorimetric estimation of microquantites of bromide (With V. A. Stenger). *J. Amer. Chem. Soc.*, 1935, **57**, 831–3.
441. "Absurdly" low concentration and the law of mass action. The ion theory. *Chem. Weekblad.* 1935, **32**, 246–9.
442. Acidimetric titration of *p*-hydroxybenzoic acid alone and in the presence of acetic acid. *J. Amer. Chem. Soc.*, 1935, **57**, 973–4.

443. Determination of strychnine and brucine as hydroferrocyanides and their separation by means of ferrocyanide (With J. J. Lingane). *J. Amer. Pharm. Assoc.*, 1934, **23**, 302–8.
444. Catalytic and induced reactions in microchemistry (With R. S. Livingston). *Ind. Eng. Chem., Analyt.*, 1935, **7**, 209–13.
445–446. Structural changes taking place during the aging of freshly formed precipitates (With Charles Rosenblum): III. *J. Amer. Chem. Soc.*, 1935, **57**, 597–600. IV. *Ibid.*, 607–11.
447. Mechanism of the aging of freshly prepared lead sulfate crystals (With Charles Rosenblum). *Phys. Rev.*, 1935, **47**, 631.
448. Calcium hypochlorite as a volumetric oxidizing agent. Stability and standardization of the solution. Determination of ammonia (With V. A. Stenger): *Ind. Eng. Chem., Analyt.*, 1935, **7**, 79–81.
49. Perfection and agglomeration of crystalline precipitates on aging. *Science*, 1936, **84**, 376–7.
450. Adsorption on ionic lattices. *J. Phys. Chem.*, 1936, **40**, 1027–40.
451. Aging of fresh precipitates in contact with a liquid medium. Irreversible flocculation of colloids. *Proc. Acad. Sci. Amsterdam*, 1937, **40**, 82–92.
452. Potassium iodide as a primary standard substance in permanganimetry (With H. A. Laitinen and J. J. Lingane). *J. Amer. Chem. Soc.*, 1937, **59**, 429–32.
453. Potentiometric iodide-silver titration at extreme dilution (With J. J. Lingane) *Ibid.*, 1936, **58**, 2457–9.
454. Detection of copper with phenolphthalein-cyanide reagent (With J. J. Lingane). *Mikrochemie Festschr. von Hans. Molisch*, 1936, 274–8.
455. The determination of the specific surface of barium sulfate (With W. M. MacNevin). *J. Amer. Chem. Soc.*, 1937, **59**, 1639–43.
456. Studies on coprecipitation and aging: XI (With B. Moskovitz). *J. Phys. Chem.*, 1937, **41**, 629–44.
457. Exchange adsorption on the surface of barium sulfate (With G. E. Noponen). *J. Amer. Chem. Soc.*, 1937, **59**, 1237–9.
458. Exchange adsorption phenomena with calcium oxalate monohydrate (With E. B. Sandell). *Ibid.*, 1937, **59**, 1643–8.
459. Electric potentials at crystal surfaces and at silver halide surfaces in particular (With H. L. Sanders). *Ibid.*, 1937, **59**, 416–20.
460. Electrode potentials of platinum, gold and silver in various solutions of electrolytes (With Chin Wang). *J. Phys. Chem.*, 1937, **41**, 539–44.
461. Volumetric determination of bromide after oxidation to bromate in the presence of much chloride (With H. Yutzy). *Ind. Eng. Chem., Analyt.*, 1937, **9**, 75–6.
462–463. Aging of fresh precipitates (With Henry C. Yutzy): XIII. *J. Amer. Chem. Soc.*, 1937, **59**, 1215–19. XIV. *Ibid.*, 1634–9.
464. Microdetermination of iodine by a catalytic method (With E. B. Sandell). *Microchim. Acta.*, 1937, **1**, 9–25.
465. Electrochemical properties of diphenylbenzidinesulfonic acid (With L. A. Sarver). *J. Amer. Chem. Soc.*, 1937, **59**, 23–5.
466. Aging of fresh precipitates: XII (With H. C. Yutzy). *Ibid.*, 1937, **59**, 916–21.
467. The aging of fresh precipitates in the presence of a liquid medium. *Osterr. Chem.-Ztg.*, 1938, **41**, 113–18.

468. The relation between equilibrium constants in water and in other solvents. Distribution coefficients of ions. *Chem. Weekblad*, 1937, **34,** 785–92.
469. Volumetric determination of bismuth as bismuth hydrogen iodide oxine (With F. S. Griffith). *Mikrochim. Acta*, 1938, **3,** 47–51.
470. Postprecipitation of nickel sulfide with copper sulfide, mercuric sulfide and zinc sulfide (With F. S. Griffith). *J. Phys. Chem.*, 1938, **42,** 541–5.
471. Postprecipitation of zinc sulfide with bismuth sulfide (With F. S. Griffith). *Ibid.*, 1938, **42,** 531–9.
472–473. Aging and properties of precipitates: XXII. (With F. S. Griffith and D. Romund Moltzau). *J. Amer. Chem. Soc.*, 1938, **60,** 1576–82. XXIII. (With F. S. Griffith). *Ibid.*, 2036–9.
474. Acid-base indicators in methanol—preliminary communication (With L. S. Guss). *Compt. rend. trav. lab. Carlsberg. Ser. chim.*, 1938, **22,** 264–71.
475. The solubility and activity coefficient of silver iodate in potassium nitrate solutions. The standard potential of the silver-silver iodate electrode (With J. J. Lingane). *J. Phys. Chem.*, 1938, **42,** 133–40.
476–481. Aging of fresh precipitates (With G. E. Noponen): XVI. *J. Amer. Chem. Soc.*, 1938, **60,** 39–41. XVII. *Ibid.*, 197–201. XVIII. *J. Phys. Chem.*, 1938, **42,** 237–43. XIX. *J. Amer. Chem. Soc.*, 1938, **60,** 499–505. XX. *Ibid.*, 505–8. XXI. *Ibid.*, 508–11.
482. Aging of precipitates: XV (With H. C. Yutzy). *Ibid.*, 1937, **59,** 2029–32.
483–484. Fundamental studies with the dropping-mercury electrode (With J. J. Lingane): I. *J. Amer. Chem. Soc.*, 1939, **61,** 825–34. II. *Ibid.*, 1045–51.
485. Calcium oxalate monohydrate as a weighing form for calcium (With E. B. Sandell). *Ind. Eng. Chem., Analyt.*, 1939, **11,** 90–3.
486. Determination of potassium with hexanitrodiphenylamine (dipicrylamine) reagent (With Gordon H. Bendix). *Ibid.*, 1939, **11,** 94–8.
487. Adsorption experiments on a sample of barium sulphate submitted by Mlle. de Brouckere (With A. A. Bushey): *Bull. Soc. chim. belges*, 1938, **47,** 689–701.
488–491. Studies in aging and coprecipitation: XXVI. (With R. T. Eggertsen). *J. Amer. Chem. Soc.*, 1939, **61,** 1036–40. XXVII. (With Roy A. Halversen). *J. Phys. Chem.*, 1939, **43,** 605–11. XXVIII. (With L. G. Overholser). *Ibid.*, 767–80. XXIX. (With L. G. Overholser). *Ibid.*, 909–22.
492. Studies on aging and formation of precipitates: XXIX (With A. S. O'Brien). *J. Chem. Phys.*, 1939, **7,** 401–4.
493. Ionization constants of acid-base indicators in methanol (With L. S. Guss). *J. Amer. Chem. Soc.*, 1938, **60,** 2516–22.
494–495. Acid-base indicators in methanol (With L. S. Guss): II. *Ibid.*, 1939, **61,** 16–19. III. *Ibid.*, 330–3.
496. Standardization of strong oxidizing agents with potassium iodide by the acetone method (With H. A. Laitinen). *Ibid.*, 1939, **61,** 1690–1.
497. The fundamental principles and applications of electrolysis with the dropping-mercury electrode and Heyrovský's polarographic method of chemical analysis (With J. J. Lingane). *Chem. Rev.*, 1939, **24,** 1–94.
498. The relation between equilibrium constants in water and in other solvents (With J. J. Lingane and W. D. Larson). *J. Amer. Chem. Soc.*, 1938, **60,** 2512–15.

499–500. Aging of precipitates (With Wm. von Fischer): XXIV. *Ibid.*, 1939, **61**, 191–4. XXV. *Ibid.*, 195–7.

501. Amperometric titrations. *Trans. Electrochem. Soc.*, 1940, **78**, 16 pp. (Preprint)

502. Cerimetric determination of small amounts of arsenic after reduction with hypophosphite reagent (With Elias Amdur). *Ind. Eng. Chem., Analyt.*, 1940, **12**, 177–9.

503. Aging and coprecipitation: XXXII (With Frank T. Eggertsen). *J. Amer. Chem. Soc.*, 1940, **62**, 2125–31.

504. Voltammetric determination of oxygen (With H. A. Laitinen). *Science.* 1940, **92**, 152–4.

505. Amperometric titrations: II (With A. Langer). *J. Amer. Chem. Soc.*, 1940, **62**, 211–18.

506. Aging and coprecipitation: XXXIII (With W. M. MacNevin). *J. Phys. Chem.*, 1940, **44**, 921–35.

507. Mixed potentials at the dropping-mercury electrode (With C. S. Miller). *J. Amer. Chem. Soc.*, 1940, **62**, 2171–4.

508–509. Aging and formation of precipitates (With A. S. O'Brien): XXX. *Ibid.*, 1939, **61**, 3409–14. XXXI. *Ibid.*, 3414–19.

510. Amperometric (polarometric) titrations: I (With Yu-Djai Pan). *Ibid.*, 1939, **61**, 3402–9.

511. Ionization constants of acid-base indicators in ethanol (With L. S. Guss). *Ibid.*, 1940, **62**, 249–51.

512. The distribution of protons between water and other solvents (With L. S. Guss). *Ibid.*, 1940, **62**, 1494–6.

513. Study of diffusion processes by electrolysis with microelectrodes (With H. A. Laitinen). *Nature*, 1939, **144**, 549–50.

514. A study of the diffusion processes by electrolysis with microelectrodes (With H. A. Laitinen). *J. Amer. Chem. Soc.*, 1939, **61**, 3344–9.

515. Polarographic study of the reduction of chromate ion at the dropping-mercury electrode (With J. J. Lingane). *Ibid.*, 1940, **62**, 852–8.

516. The silicon carbide electrode (With D. N. Hume). *Ibid.*, 1941, **63**, 2805–6.

517. Photovoltaic behavior of pure silver bromide (With Herbert L. Sanders). *J. Phys. Chem.*, 1940, **44**, 936–43.

518. Chemistry of vitamin E: XXIX (With Lee Irvin Smith, Stanley Wawzonek and P. M. Ruoff). *J. Amer. Chem. Soc.*, 1941, **63**, 1018–24.

519. The anodic reaction and waves of cysteine at the dropping-mercury electrode and at the platinum micro wire electrode (With Cyrus Barnum). *Ibid.*, 1940, **62**, 3061–5.

520. The reduction of cystine at the dropping-mercury electrode (With Cyrus Barnum) ' *Ibid.*, 1941, 520–6.

521. Studies on aging and coprecipitation: XXXIV (With F. T. Eggertsen). *Ibid.*, 1941, **63**, 1412–18.

522–524. Amperometric titrations: III. (With H. A. Laitinen). *Rec. Trav. chim.*, 1940, **59**, 922–8. V. (With A. Langer). *J. Amer. Chem. Soc.*, 1940, **62**, 3172–5 (1940). VI. (With Yu-Djai Pan). *Ibid.*, 332–5.

525. The reduction of oxygen at the dropping-mercury electrode (With C. S. Miller). *Ibid.*, 1941, **63**, 1013–17.

526. Anodic waves involving electro-oxidation of mercury at the dropping-mercury electrode (With C. S. Miller). *Ibid.*, 1941, **63**, 1405–11.
527. Current voltage curves of mercurous and mercuric salts at the dropping-mercury electrode (With C. S. Miller). *Ibid.*, 1941, **63**, 2732–4.
528. The reduction of sulfurous acid (sulfur dioxide) at the dropping-mercury electrode (With C. S. Miller). *Ibid.*, 1941, **63**, 2818–21.
529. The use of the dropping-mercury electrode as an indicator electrode in poorly poised systems (With E. F. Orlemann). *Ibid.*, 1941, **63**, 664–7.
530. An application of the Ilkovič equation to the analysis of mixtures of reducible substances with the dropping-mercury electrode (With E. F. Orlemann). *Ibid.*, 1941, **63**, 2085–8.
531. A quantitative expression for the extractability of metals in the form of dithizonates from aqueous solutions. The equilibrium constant of zinc dithizonate. Preliminary paper (With E. B. Sandell). *Ibid.*, 1941, **63**, 1906–8.
532. Factors to be considered in quantitative polarography. *Ind. Eng. Chem., Analyt.* 1942, **14**, 195–200.
533. Amperometric titrations. Amperometric determination of phosphate with uranyl acetate (With Gunter Cohn). *Ibid.*, 1942, **14**, 412–18.
534–535. Aging and coprecipitation (With F. T. Eggertsen): XXXV. *J. Phys. Chem.*, 1942, **46**, 458–63. XXXVI. *Ibid.*, 616–20.
536. Elimination of the water wave in polarographic work at relatively high indifferent electrolyte concentrations (With E. F. Orlemann). *Ind. Eng. Chem., Analyt.*, 1942, **16**, 321–3.
537. The solubility of lead sulfate and of lead oxalate in various media (With R. W. Perlich and D. Weiblen). *J. Phys. Chem.*, 1942, **46**, 561–70.
538. Voltammetric determinations and amperometric titrations with a rotating microelectrode of platinum wire (With H. A. Laitinen). *Ibid.*, 1941, **45**, 1079–93.
539. Voltammetry with stationary microelectrodes of platinum wire (With H. A. Laitinen). *Ibid.*, 1941, **45**, 1061–79.
540. Potassium iodide for use as a primary standard (With J. J. Lingane). *Inorganic Syntheses*, 1939, **1**, 163–5.
541. The anomalous electroreduction of water at the dropping-mercury electrode in relatively concentrated salt solutions (With E. F. Orlemann). *J. Amer. Chem. Soc.*, 1942, **64**, 833–8.
542. The reaction of iodate and bromate in acid medium at the dropping-mercury electrode (With E. F. Orlemann). *Ibid.*, 1942, **64**, 1044–52.
543. The reduction of iodate and bromate at the dropping-mercury electrode in neutral and basic media and the effects of salts on the current-voltage curves (With E. F. Orlemann). *Ibid.*, 1942, **64**, 1970–7.
544–545. Chemistry of vitamin E (With Lee Irvin Smith and Leo J. Spillane): XXXVI. *Ibid.*, 1942, **64**, 644–5. XXXVII. *Ibid.*, 646–8.
546. Chemistry of vitamin E: XXXV (With Lee Irvin Smith and Leo J. Spillane). *Ibid.*, 1942, **64**, 447–51.
547. The validity of the Ilkovič equation in the polarographic analysis of alkali metals and the characteristics of the alkali waves in various media (With Ignace Zlotowski). *Ibid.*, 1942, **64**, 1297–1301.

548. Polarographic determination of potassium, sodium and lithium (With Ignace Zlotowski). *Ind. Eng. Chem., Analyt.*, 1942, **14,** 473–7.
549. Polarographic determination of potassium, sodium and lithium (With Ignace Zlotowski). *Ibid.*, 1942, **14,** 473–7.
550. Determination of pyrophosphate by precipitation with cadmium and polarographic measurement of cadmium in the precipitate (With Gunther Cohn). *Ibid.*, 1942, **14,** 886–90.
551. Determination of calcium by precipitation with picrolonic acid and polarographic measurement of the residual picrolonic acid (With Gunther Cohn). *J. Biol. Chem.*, 1943, **147,** 705–9
552. Amperometric titration of picrolonic acid and indirect volumetric determination of calcium by precipitation as picrolonate and back titration of the excess of picrolonic acid with methylene blue (With Gunther Cohn). *Ibid.*, 1943, **148,** 711–18.
553. Aging and coprecipitation: XXXVII (With C. W. Carr). *J. Phys. Chem.*, 1943, **47,** 148–52.
554. Determination of iodate in the presence of bromate and chlorate (With David N. Hume). *Ind. Eng. Chem., Analyt.*, 1943, **15,** 174–5.
555. The attachment and detachment of dropping mercury under various conditions (With G. J. Kahan). *J. Amer. Chem. Soc.*, 1942, **64,** 2553–7.
556. Polarographic determination of manganese as tri-dihydrogen pyrophosphatomanganate (With J. I. Watters). *Ind. Eng. Chem., Analyt.*, 1943, **15,** 8–13.
557. The Lewis and the Brönsted-Lowry definitions of acids and bases. *J. Phys. Chem.*, 1944, **48,** 51–7.
558. A new method for the polarographic determination of nitrate (With W. E. Harris and G. Matsuyama). *J. Amer. Chem. Soc.*, 1944, **66,** 1782–6.
559. The behavior of SO_2 as an acid in MeOH (With L. S. Guss). *Ibid.*, 1944, **66,** 1484–8.
560. A revision of the oxidation potentials of the *o*-phenanthroline- and bipyridylferrous complexes (With David N. Hume). *Ibid.*, 1943, **65,** 1895–7.
561. The oxidation potential of the chromocyanide-chromicyanide couple and the polarography of the chromium cyanide complexes (With David N. Hume). *Ibid.*, 1943, **65,** 1897–1901.
562. Iodometric determination of iodates, bromates or permanganates in the presence of copper (With David N. Hume). *Ind. Eng. Chem., Analyt.*, 1944, **16,** 103–4.
563. Polarographic studies of sulfonamides: I (With Nathan I. Levitan, Wm. G. Clark and Daniel J. Tenenberg). *J. Amer. Chem. Soc.*, 1943, **65,** 2265–8.
564. Determination of manganese after oxidation to tri-dihydrogen pyrophosphatomanganate (With J. I. Watters). *Ind. Eng. Chem., Analyt.*, 1944, **16,** 187–9.
565. Polarographic behavior of alkaline earth metals: I (With I. Zlotowski). *J. Amer. Chem. Soc.*, 1944, **66,** 1431–5.
566. The polarography of uranium: I (With W. E. Harris). *Ibid.*, 1945, **67,** 1484–90.
567. The mechanism of emulsion polymerizations: I (With W. J. Dale). *Ibid.*, 1945, **67,** 1672–4.
568. Aging of crystalline precipitates. *Suomen Kem.*, 1943, **16A,** 89–96.
569. Amperometric titration of mercaptans with silver nitrate using the rotating platinum electrode (With W. E. Harris). *Ind. Eng. Chem., Analyt.*, 1946, **18,** 161–2.

570. The polarography of uranium: II (With W. E. Harris). *J. Amer. Chem. Soc.*, 1946, **68,** 1175–9.

571. Solubilization of *p*-dimethylaminoazobenzene in soap solutions (With W. F. Johnson). *J. Phys. Chem.*, 1946, **50,** 440–2.

572. Assay of hydroquinone (With Thomas S. Lee). *Ind. Eng. Chem., Analyt.*, 1946, **18,** 452.

573. Polarographic analysis of aluminum alloys (for iron, copper, lead, nickel and zinc) (With Geo. Matsuyama). *Ibid.*, 1945, **17,** 615–20.

574. Amperometric microtitration of very dilute chromate solutions using the rotating platinum electrode (With D. R. May). *Ind. Eng. Chem., Analyt.*, 1946, **18,** 208–9.

575. Determination of alkyl disulfides in the absence and presence of mercaptans (With D. R. May, Perry Morgan, H. A. Laitinen and A. S. O'Brien). *Ibid.*, 1946, **18,** 442–4.

576. Polarographic behavior of alkaline earth metals: II (With I. Zlotowski). *J. Phys. Chem.*, 1945, **49,** 386–405.

577. Determination of polystyrene in GR-S rubber (With T. S. Lee and C. W. Carr). *J. Polymer Sci.*, 1946, **1,** 429–33.

578. Determination of persulfate in emulsion polymerization latexes (With L. S. Guss, D. R. May and A. I. Medalia). *Ibid.*, 1946, **1,** 340–52.

579. Aging of precipitates and coprecipitation: XXXIX (With I. Shapiro). *J. Chem. Phys.*, 1947, **15,** 41–6.

580. The electrokinetic potentials of precipitates (With L. H. Reyerson and Keith Coad). *J. Phys. Colloid Chem.*, 1947, **51,** 321–32.

581. The mechanism of emulsion polymerizations: II (With W. J. Dale). *J. Amer. Chem. Soc.*, 1947, **69,** 441–6.

582. The polarography of uranium: III (With W. E. Harris). *Ibid.*, 1947, **69,** 446–51.

583. The aging of precipitates and coprecipitation: XXXVIII (With I. Shapiro). *J. Phys. Colloid Chem.*, 1947, **51,** 483–93.

584–587. Thiols as promoters and modifiers in emulsion copolymerization of butadiene and styrene using potassium persulfate as catalyst (With W. E. Harris): I. *J. Polymer Sci.*, 1947, **2,** 41–8. II. *Ibid.*, 49–71. III. *Ibid.*, 72–81. IV. *Ibid.*, 82–9.

588–590. Use of perbenzoic acid in analysis of unsaturated compounds: I. (With Thomas S. Lee and Mary Anne Mairs). *Ibid.*, 1947, **2,** 199–205. II. (With Thomas S. Lee). *Ibid.*, 206–19. III. (With Thomas S. Lee and Mary Anne Mairs). *Ibid.*, 220–8

591. The use of membrane electrodes in the study of soap solutions (With C. W. Carr and W. F. Johnson). *J. Phys. Colloid Chem.*, 1947, **51,** 636–44.

592. Amperometric titration of styrene with potassium bromate using the rotating platinum electrode (With F. A. Bovey). *Analyt. Chem.*, 1947, **19,** 498–500.

593. The mechanism of emulsion polymerization: III. Oxygen as a comonomer in the emulsion polymerization of styrene (With F. A. Bovey). *J. Amer. Chem. Soc.*, 1947, **69,** 2143.

594. Ethanol-toluene-water as solvent mixture for extraction of nonpolymer from R-SG (With C. W. Carr and Betty J. Carr). *J. Polymer Sci.*, 1947, **2,** 637.

595. Laurate-ion activity in solutions of potassium laurate in the absence and presence of neutral salts (With Warren F. Johnson). *J. Phys. Colloid Chem.*, 1948, **52,** 22.
596. Determination of unsaturation of synthetic and natural rubbers by means of iodine monochloride (With T. S. Lee and Mary Anne Mairs). *J. Polymer Sci.*, 1948, **3,** 66.
597. Studies of retarders and inhibitors in the emulsion polymerization of styrene: I. Retarders (With F. A. Bovey). *J. Amer. Chem. Soc.*, 1948, **70,** 791.
598. Combination of potassium ferricyanide, diazothio-ether and mercaptan as "catalyst" for emulsion polymerizations of butadiene and styrene (With W. J. Dale). *J. Polymer Sci.*, 1948, **3,** 400.
599. Polarographic behavior of phenolphthalein (With D. J. Lehmicke). *J. Amer. Chem. Soc.*, 1948, **70,** 1879.
600. Polarographic behavior of nitrosophenylhydroxylamine (With A. Liberti). *Ibid.*, 1948, **70,** 1885.
601. Studies on the aging of precipitates and coprecipitation: XL. The solubility of lead chromate as a function of the particle size (With D. R. May). *J. Phys. Colloid Chem.*, 1948, **52,** 836.
602. Solubilization of dimethylaminoazobenzene in solutions of detergents: I. The effect of temperature on the solubilization and upon the critical concentration (With W. Stricks). *Ibid.*, 1948, **52,** 915.
603. Studies on aging of precipitates and coprecipitation: XLI. The bulkiness and porosity of silica powder (With I. Shapiro). *Ibid.*, 1948, **52,** 1020.
604. Inhibition and retardation of vinyl polymerization (With F. A. Bovey). *Chem. Rev.*, 1948, **42,** 491.
605. Reaction of ferrous and ferric iron with 1,10-phenanthroline: I. Dissociation constants of ferrous and ferric phenanthroline (With T. S. Lee and D. L. Leussing). *J. Amer. Chem. Soc.*, 1948, **70,** 2348.
606. Potentiometric investigation of tripyrophosphatomanganic(III) acid (With James I. Watters). *Ibid.*, 1948, **70,** 2455.
607. Accumulation of traces of arsenate by coprecipitation with magnesium ammonium phosphate (With C. W. Carr). *Analyt. Chem.*, 1948, **20,** 728.
608. Reaction of ferrous and ferric iron with 1,10-phenanthroline: II. Kinetics of formation and dissociation of phenanthroline (With T. S. Lee and D. L. Leussing). *J. Amer. Chem. Soc.*, 1948, **70,** 3596.
609. Studies on aging of precipitates and coprecipitation: XLII. Aging of silver bromide in the dry state (With I. Shapiro). *J. Phys. Colloid Chem.*, 1948, **52,** 1319.
610. Polarographic and amperometric determination of barium (With H. P. Gregor). *Analyt. Chem.*, 1948, **20,** 541.
611. Thermal aging of silica. *Festskr. J. Arvid. Hedvall* (With Gunther Cohn). 1948, 97.
612. Beginning course in quantitative analysis. *J. Chem. Educ.*, 1948, **25,** 597.
613. Amperometric titrations. *Analyt. Chim. Acta*, 1948, **2,** 606–621.
614. Equilibrium and kinetic studies on the formation and dissociation of ferroïn and ferriïn (With T. S. Lee and D. L. Leussing). *Analyt. Chem.*, 1948, **20,** 985.
615. Indicators. *Ibid.*, 1949, **21,** 101.

616. Polarographic determination of the molecular weight of serum albumin by its effect on the diffusion current of methyl orange (With W. Stricks). *J. Amer. Chem. Soc.*, 1949, **71**, 1519.
617. Solubilization of dimethylaminoazobenzene in solutions of detergents: II. Effect of electrolytes on the critical concentration and the solubilization of dimethylaminoazobenzene, orange OT, and transazobenzene in detergent solutions (With W. Stricks). *J. Phys. Colloid Chem.*, 1949, **53**, 424–454.
618. A polarographic study of cobalt cyanide complexes (With David N. Hume). *J. Amer. Chem. Soc.*, 1949, **71**, 867.
619. Physicochemical principles in analytical research. *Chem. Eng. News.* 1949, **27**, 835. (*a*) Translation of the above published in *Information de Quimicá Analiticá.* Vol. III, No. 6, pp. 183–192 (Nov. Dec., 1949).
620. Polarographic determination of pentavalent antimony in the presence of pentavalent arsenic (With R. L. Probst). *Analyt. Chem.*, 1949, **21**, 753.
621. Amperometric determination of primary and tertiary mercaptans in their mixtures (With W. E. Harris). *Ibid.*, 1949, **21**, 963.
622. Polarographic procedure for determination of cobalt as cobalt(III) ammine. (With J. I. Watters). *Ibid.*, 1949, **21**, 1466.
623. The reaction between ferrous iron and peroxides: I. Reaction with hydrogen peroxide in the absence of oxygen (With A. I. Medalia). *J. Amer. Chem. Soc.*, 1949, **71**, 3777.
624. The reaction between ferrous iron and peroxides: II. Reaction with hydrogen peroxide in the presence of oxygen (With A. I. Medalia). *Ibid.*, 1949, **71**, 3784.
625. The reaction between ferrous iron and peroxides: III. Reaction with cumene hydroperoxide in aqueous solution (With A. I. Medalia). *Ibid.*, 1949, **71**, 3789.
626. Redox Recipes: I. Reaction between ferrous iron and peroxides. General consideration (With A. I. Medalia). *J. Polymer Sci.*, 1949, **4**, 377–398.
627. Determination of disappearance of bis-isopropyl Xanthogen (Dixie) in synthetic rubber latex during polymerization (With D. R. May). *J. Polymer Sci.*, 1949, **4**, 735–743.
628. Indicators. *Analyt. Chem.*, 1950, **22**, 65.
629. The polarography of chloroform and carbon tetrachloride (With T. S. Lee, D. Stocescova, and E. P. Parry). *Ibid.*, 1950, **22**, 521.
630. Determination of unsaturation of butyl rubbers and certain branched olefins. Iodine monochloride method (With T. S. Lee and Ethel Johnson). *Ibid.*, 1950, **22**, 995.
631. Determination of free carbon in cured rubber stocks (With R. G. Gutmacher). *Ibid.*, 1950, **22**, 1002.
632. Polarographic determination of cobalt as trioxalatocobaltate(III) (With J. I. Watters). *Ibid.*, 1950, **22**, 1422.
633. Analytical chemistry as a technique and as a science. *Chem. Eng. News*, 1950, **28**, 2882.
634. Studies on aging of precipitates and coprecipitation: XLIII. Thermal aging of precipitated silica (silica gel) (With I. Shapiro) *J. Amer. Chem. Soc.*, 1950, **72**, 776.
635. Argentometric amperometric titration of cysteine and cystine (With W. Stricks). *Ibid.*, 1950, **72**, 1952.

636. Reaction of ferrous and ferric iron with 1,10-phenanthroline: III. The ferrous monophenanthroline complex and the colorimetric determination of phenanthroline (With D. L. Leussing and T. S. Lee). *Ibid.*, 1950, **72,** 2173.
637. The locus of the initiation in an emulsion polymerization recipe containing ferrous iron and benzoyl peroxide (With Madolyn Youse). *Ibid.*, 1950, **72,** 3431.
638. The polarography of nickel cyanide complexes and the solubilities and constitution of nickel cyanide (With D. N. Hume). *Ibid.*, 1950, **72,** 4423.
639. Mikro-Drahtelektroden in Der Polarographie and Bei Amperometrischen Titrationen. (Micro-wire electrodes in polarography and amperometric titrations) (With D. L. Leussing and Gustav F. Hüttig). *Z. Anorg. Chem.*, 1950, **262,** 160.
640. The sorption of GR-S type rubber by carbon black: I. Sorption from benzene solution by Graphon (With A. Kahn). *J. Phys. Colloid Chem.*, 1950, **54,** 251.
641. Studies on the rate of the emulsion polymerization of butadiene-styrene (75:25) as a function of the amount and kind of emulsifier used: I. Polymerizations with commercial and pure soaps (With C. W. Carr, E. J. Meehan, and R. J. Stenberg). *J. Polymer Sci.*, 1950, **5,** 101.
642. Studies on the rate of the emulsion polymerization of butadiene-styrene (75:25) as a function of the amount and kind of emulsifier used: II. Polymerization with fatty acid soaps, rosin soaps and various synthetic emulsifiers (With C. W. Carr, E. J. Meehan and D. E. Williams). *Ibid.*, 1950, **5,** 201.
643. The potassium ferricyanide-diazothio-ether-mercaptan recipe for emulsion polymerization of butadiene and styrene: II. Effect of some chemical variables (With W. J. Dale). *Ibid.*, 1950, **5,** 301.
644. Redox recipes: II. Redox recipes in alkaline medium initiated by the system cumene hydroperoxide-iron-sugar at 30° (With A. I. Medalia). *Ibid.*, 1950, **5,** 391.
645. The mechanism of emulsion polymerization: IV. Kinetics of polymerization of styrene in water and detergent solutions (With F. A. Bovey). *Ibid.*, 1950, **5,** 487.
646. Studies of retarders and inhibitors in the emulsion polymerization of styrene: II. Inhibitors (With F. A. Bovey). *Ibid.*, 1950, **5,** 569.
647. The potassium ferricyanide-diazothioether-mercaptan recipe for emulsion polymerization of butadiene and styrene: III. Determination of *p*-methoxyphenyl diazothio-(2-naphthyl) ether (With W. J. Dale and I. K. Miller). *Ibid.*, 1950, **5,** 667.
648. Polarographic investigations of reactions in aqueous solutions containing copper and cysteine (With W. Stricks). *Analyt. Chem.*, 1951, **23,** 763.
649. Argentometric amperometric titration of traces of chloride with the rotated platinum electrode as indicator electrode (With P. K. Kuroda). *Ibid.*, 1951, **23,** 1306.
650. Determination of traces of chloride by potentiometric titration to the apparent equivalence potential (With P. K. Kuroda). *Ibid.*, 1951, **23,** 1304.
651. Polarographic determination of cobalt as trioxalatocobaltate (III) (With J. I. Watters). *Ibid.*, 1950, **22,** 1422.
652. Analysis of mixtures based on rates of reaction (With T. S. Lee). *Ann. Sci.*, 1951, **53,** 1093.

653. The chemistry of persulfate: II. The reaction of persulfate with mercaptans solubilized in solutions of saturated fatty acid soaps (With I. K. Miller). *J. Amer. Chem. Soc.*, 1951, **73**, 5118.
654. Catalytic polarographic waves of hydrogen peroxides: II. Kinetic waves for the peroxy compounds of molybdenum^{VI}, tungsten^{VI} and vanadium^{V} (With E. P. Parry). *Ibid.*, 1951, **73**, 5315.
655. Catalytic polarographic waves of hydrogen peroxide: I. The kinetic wave for the ferric iron-hydrogen peroxide system (With E. P. Parry). *Ibid.*, 1951, **73**, 3718.
656. The reaction between ferrous iron and peroxides: IV. Reaction with potassium persulfate. *Ibid.*, 1951, **73**, 1733.
657. The chemistry of persulfate: I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium (With I. K. Miller). *Ibid.*, 1951, **73**, 3055.
658. Determination of the degree of dissociation of micelles of 1-n-dodecanesulfonic acid by use of the acid catalyzed reaction between iodine and acetone (With W. F. Johnson). *Ibid.*, 1951, **73**, 4563.
659. Equilibrium constants of the reaction of sulfite with cystine and with dithiodiglycolic acid (With W. Stricks). *Ibid.*, 1951, **73**, 4569.
660. Ferric iron with 1,10-phenanthroline: IV. Application to investigation of zinc phenanthroline complexes (With D. L. Leussing and T. Lee). *Ibid.*, 1951, **73**, 390.
661. Polarographic investigations of reactions in aqueous solution containing copper and cysteine: I. Cuprous copper and cysteine in ammoniacal medium (With W. Stricks). *Ibid.*, 1951, **73**, 1723.
662. Polarographic investigations of reactions in aqueous solutions containing copper and cysteine: II. Reaction in ammoniacal medium in the presence and absence of sulfite (With W. Stricks). *Ibid.*, 1951, **73**, 1728.
663. Amperometric titration of Sn^{IV} and Hg^{II} with tetraphenylarsonium chloride (With B. A. Johnson). *J. Electrochem. Soc.*, 1951, **98**, 231.
664. Amperometric titrations with s-nitrophenylarsonic acid (With B. A. Johnson). *Ibid.*, 1951, **93**, 138.
665. Cosolubilization in solutions of potassium laurate. Effect of co-solubilized alcohol and hydrocarbons on the solubilization of several aromatic compounds in potassium laurate solutions. *J. Phys. Colloid Chem.*, 1951, **55**, 699.
666. Sorption of GR-S type rubber black: II. Effect of variables on the sorption of Craphan (With A. G. Gutmacher and A. Kahn). *Ibid.*, 1951, **55**, 1240.
667. Redox recipes: IV. Dihydroxyacetone recipes at 0°C (With A. I. Medalia). *J. Polymer Sci.*, 1951, **6**, 189.
668. Redox recipes: III. Use of various sugars at 0°C and 30°C in a cumene hydroperoxide-iron sugar recipe (With A. I. Medalia). *Ibid.*, 1951, **6**, 93.
669. Redox recipes: V. Redox system, ferrous sulfide-cumene hydroperoxide (With A. I. Medalia). *Ibid.*, 1951, **6**, 209.
670. Studies on rate of emulsion polymerization of butadiene styrene 75:25 as a function of amount and kind of emulsifier used: III. Effect of amount of soap on rate of polymerization (With E. J. Meehan and E. M. Carr). *Ibid.*, 1951, **6**, 73.

671. Determination of nicrogel in GR-S rubber (With A. I. Medalia). *Ibid.*, 1951, **6,** 433.
672. Studies on the rate of emulsion polymerization of butadiene-styrene (75:25) as a function of the amount and kind of emulsifier used with persulfate as activator: IV. Addition of emulsifier during reaction. Seeding effects (With E. J. Meehan and E. M. Carr). *Ibid.*, 1951, **6,** 577.
673. Electrolytic initiation of polymerization (With L. Ferstanding). *Ibid.*, 1951, **6,** 963.
674. Polarography of tin^{IV} in presence of traces of tetraphenylarsonium chloride (With R. A. Johnson). *Analyt. Chem.*, 1951, **23,** 574.
675. Determination of organic peroxides by reaction with ferrous iron (With A. I. Medalia). *Ibid.*, 1951, **23,** 595.
676. Solubilization of dodecylammonium thiosulfate in dodecylammonium bromide solution at 50° (With W. F. Johnson). *J. Amer. Chem. Soc.*, 1952, **74,** 20.
677. A study of the reaction between dodecylbromide and thiosulfate ion solutions of dodecylammonium bromide (With W. F. Johnson). *Ibid.*, 1952, **74,** 22.
678. Anodic and cathodic voltammetry of thallium at the rotated platinum wire electrode (With J. Jordan). *Ibid.*, 1952, **74,** 382.
679. Studies on the system iron-ethylenediaminetetra-acetate (With Clemens Auerbach). *Ibid.*, 1952, **74,** 1452.
680. Oxygen induced electroreduction of hydrogen peroxide at rotating platinum electrode (With J. Jordan). *Ibid.*, 1952, **74,** 570.
681. Amperometric titrations. *Jubilaire*, 1897–1947, pp. 127–144 (Belgrade, Yugoslavia).
682. Kinetic (catalytic) currents for systems containing hydrogen peroxide (With E. P. Parry). *International Polarographic Congress* (*Prague*), 1951, **1,** 145–154.
683. Formation of bound rubber of GR-S type polymers with carbon black. (With J. Duke and W. K. Taft) *Ind. Eng. Chem.*, 1951, **43,** 2885.
684. Polarographic protein tests with milk (With W. Stricks). *International Polarographic Congress* (*Prague*), 1951, **1,** 386.
685. Das polarographische Verhalten von Ti(III) and Ti(IV) in Athylendiamintetraazetat (With M. Blumer). *Experientia*, 1952, VIII/4 138.
686. Exaltation of the limiting current of oxygen by hydrogen peroxide at the rotated gold electrode as a means for amperometric determination of traces of oxygen (With J. Jordan). *Analyt. Chem.*, 1952, **24,** 1071.
687. The reduction of carbon disulfide at the dropping mercury electrode (With P. E. Toren and R. W. Ramette). *Ibid.*, 1952, **24,** 1037.
688. Sorption of GR-S type of polymer on carbon black: III. Sorption by commercial blacks (With R. G. Gutmacher). *J. Phys. Chem.*, 1952, **56,** 570.
689. Chemistry of persulfate. III. Reaction of persulfate with mercaptan solubilized in sodium laurate solution in the presence of unsaturated compounds (With E. J. Meehan). *J. Amer. Chem. Soc.*, 1952, **74,** 4419.
690. Polarography of glutathione (With W. Stricks). *Ibid.*, 1952, **74,** 4646.
691. Redox recipes: VI. Redox systems containing potassium chromate as oxidizing constituent (With E. J. Meehan). *J. Polymer Sci.*, 1952, **9,** 327–342.
692. Redox recipes: VII. A recipe with ferric versenate, hydrazine and hydroperoxide as activating system (veroxazine recipe) (With E. J. Meehan). *Ibid.*, 1952, **9,** 343.

693. Redox recipes: VIII. A recipe with ferric versenate, sodium sulfide and hydroperoxide as activating system (veroxasulfide recipe) (With E. J. Meehan). *Ibid.*, 1952, **9**, 433–52.
694. Oxygen induced electroreduction of hydrogen peroxide and reduction of oxygen at the rotated gold wire electrode (With J. Jordan). *J. Amer. Chem. Soc.*, 1952, **74**, 4801.
695. Aging of crystalline precipitates. *Analyst*, 1952, **77**, 1000–1011.
696. Determination of osmium (With E. P. Parry). *Analyt. Chem.*, 1953, **25**, 188.
697. Volumetric determination of persulfate in the presence of organic substances (With E. M. Carr). *Ibid.*, 1953, **25**, 298.
698. Mechanism of initiation of emulsion polymerization by persulfate (With E. J. Meehan and E. M. Carr). *J. Amer. Chem. Soc.*, 1953, **75**, 1439.
699. Acid strength of iodine monochloride, antimony trichloride and picric acid with reference to the bases pyridine and aniline in nitrobenzene (With D. Stocesova and T. S. Lee). *J. Amer. Chem. Soc.*, 1953, **75**, 1834.
700. Voltammetry of iodine and iodide at rotated platinum wire electrodes (With J. Jordan). *Ibid.*, 1953, **75**, 1571–5.
701. Polarography of nitroprusside. Equilibrium constant of the reaction between nitroprusside and hydroxyl ions (With P. E. Toren). *Ibid.*, 1953, **75**, 1197–1201.
702. Voltammetric determination of lead as lead dioxide at the rotated platinum wire electrode (With J. Jordan and A. Heyndrickx). *Analyt. Chem.*, 1953, **25**, 884–87.
703. Redox recipes: IX. Alkaline nitroprusside-hydroperoxide recipes (With E. J. Meehan). *J. Polymer Sci.*, 1953, **9**, 71–82.
704. Solubility product of ferrous hydroxide and the ionization of the aquo-ferrous ion (With D. L. Leussing). *J. Amer. Chem. Soc.*, 1953, **75**, 2476–77.
705. Polarography of thioglycolic acid (With D. L. Leussing). *J. Electrochem. Soc.*, 1953, **100**, 334–8.
706. Amperometric titration of oxidized glutathione in presence of cystine (With W. Stricks). *Analyt. Chem.*, 1953, **25**, 1050–57.
707. Experimental study of the polarographic cancer test and of the sulfhydryl titration for the differentiation between normal, cancerous and other pathological sera (With W. Stricks, D. G. Bush, and P. K. Kuroda). *Lancet*, 1953, **73**, 328–35.
708. Iron-thioglycolate complexes (With D. L. Leussing). *J. Amer. Chem. Soc.*, 1953, **75**, 3904–11.
709. The amperometric titration of traces of ammonia with hypobromite at the rotated platinum wire electrode (With W. Stricks and L. Morren). *Analyst*, 1953, **78**, 405–414.
710. Electrodes with convection controlled limiting currents (convection electrodes) (With J. Jordan). *J. Amer. Chem. Soc.*, 1953, **75**, 4869.
711. The polarographic serum reaction and the amperometric sulphydryl titration for the detection of cancer. The sulphydryl content of normal and of cancerous blood serum. *Pharm. Weekblad*, 1953, **88**, 733–44.
712. Reactions between mercuric mercury and cysteine and glutathione. Apparent dissociation constants, heats and entropies of formation of various forms of mercuric mercapto-cysteine and -glutathione (With W. Stricks). *J. Amer. Chem Soc.*, 1953, **75**, 5673–81.

713. Amperometric titration and voltammetric determination of iodide with rotated platinum wire indicator electrode (With J. Jordan). *Analyt. Chem.*, 1953, **25,** 1833–7.
714. Effect of detergent on the polymerization of allyl acetate (With E. J. Meehan, E. M. Carr). *J. Polymer Sci.*, 1954, **13,** 113–21.
715. Polarographic and amperometric mercurometric determination of disulfide groups in cystine, oxidized glutathione, and proteins (With W. Stricks and N. Tanaka). *Analyt. Chem.*, 1954, **26,** 299.
716. Amperometric mercurimetric titration of sulfhydryl groups in biologically important substances at the rotated platinum wire electrode as indicator electrode (With W. Stricks and L. Morren). *Ibid.*, 1954, **26,** 366.
717. Studies on aging and coprecipitation: XLIV. Aging of silver bromide in the colloidal state (With R. C. Bowers). *J. Amer. Chem. Soc.*, 1954, **76,** 1503–9.
718. Formation and properties of various mercuric mercapto thioglycolates formed in reactions between mercuric mercury and thioglycolic acid (With W. Stricks and A. Heyndrickx). *Ibid.*, 1954, **76,** 1515–19.
719. Studies on aging and coprecipitation: XLV. The irreversible flocculation of colloidal silver bromide and the aging in the flocculated state (With R. C. Bowers). *Ibid.*, 1954, **76,** 1510–15.
720. Rotated and stationary platinum wire electrodes. Residual current-voltage curves and dissolution patterns in supporting electrolytes (With Nobuyuki Tanaka). *Analyt. Chem.*, 1954, **26,** 632–636.
721. Nitrogen, sulfhydryl, and disulfide contents in normal and cancer sera and in their albumin and globulin fractions. Action sulfite on disulfide groups in normal and cancer sera (With W. Stricks, Loes Morren, and A. Heyndrickx). *J. Natl. Cancer Inst.*, 1954, **14,** 1233–45.
722. Convection controlled limiting currents (convection currents): I. The platinum wire convection electrode (With J. Jordan). *J. Amer. Chem. Soc.*, 1954, **76,** 3843–45.
723. Convection controlled limiting currents (convection currents: II. The convection mercury electrode (With J. Jordan and S. Prager). *Ibid.*, 1954, **76,** 5221–25.
724. Relations between voltammetry and potentiometric and amperometric titrations. *Analyt. Chem.*, 1954, **26,** 1685–91.
725. Anodic polarographic wave of vanadium$^{\mathrm{IV}}$ aged in alkaline solution (With P. T. Toren). *Ibid.*, 1954, **26,** 1361.
726. Mechanism of emulsion polymerization of styrene with persulfate as activator in the absence and presence of mercaptan and a retarder (With P. R. O'Connor and J. L. Hansen). *J. Polymer Sci.*, 1955, **15,** 459–73.
727. The use of rotating and stationary electrodes for fast reactions (With W. L. Reynolds). *Faraday Soc. Discussion*, 1954, **17,** 167–73.
728. Apparent transfer constants of mercaptans in emulsion polymerization: I. Role of diffusion and distribution coefficients (With E. J. Meehan and P. R. Sinha). *J. Polymer Sci.*, 1955, **18,** 471–82.
729. Iron-cysteinate complexes (With N. Tanaka and W. Stricks). *J. Amer. Chem. Soc.*, 1955, **77,** 1996–2004.
730. Oxidation of ferrous cysteinate complex by cystine. Oxidation potential of the cystine-cysteine system (With N. Tanaka and W. Stricks). *Ibid.*, 1955, **77,** 2004–2006.

731. Equilibrium constants of the reaction between sulfite and oxidized glutathione (With W. Stricks and R. C. Kapoor). *Ibid.*, 1955, **77**, 2057–2061.
732. *N,N'*-Dihydroxyethylglycine and its complexes with iron (With P. E. Toren). *Ibid.*, 1955, **77**, 2061–2064.
733. Halide films at the convection mercury electrode (With J. Jordan). *Ibid.*, 1955, **77**, 3215–16.
734. Equilibrium constants of exchange reactions of cystine with glutathione and with thioglycolic acid both in the oxidized and reduced state (With W. Stricks and R. C. Kapoor). *Ibid.*, 1955, **77**, 4733–39.
735. The polarographic prewaves of cystine (RSSR) and dithiodiglycolic acid (TSST) and the oxidation potentials of the systems RSSR-RSH and TSST-TSH (With W. Stricks and Noboyuki Tanaka). *Ibid.*, 1955, **77**, 4739–42.
736. Polarographic reduction of cystine and of dithiodiglycolic acid in the presence of iron (With W. Stricks and Nobuyuki Tanaka). *Ibid.*, 1955, **77**, 5215–18.
737. The anodic waves of cysteine at the convection and dropping mercury electrodes (With W. Stricks and Nobuyuki Tanaka). *Ibid.*, 1955, **77**, 5211–15.
738. Voltammetry of silver halide suspensions and amperometric titration of halides (With J. T. Stock). *Analyst*, 1955, **80**, 860–870.
739. Acid-base equilibria in glacial acetic acid: I. Spectrophotometric determination of acid and base strengths and of some dissociation constants (With S. Bruckenstein). *J. Amer. Chem. Soc.*, 1956, **78**, 10.
740. Acid-base equilibria in glacial acetic acid: II. Spectrophotometric determination of the ionization and dissociation constants of p,p'-dimethylaminoazobenzene and pyridine. The abnormal effect of water on indicator bases (With S. Bruckenstein). *J. Amer. Chem. Soc.*, 1956, **78**, 109.
741. Instrumental methods in analytical curricula. *J. Chem. Educ.*, 1956, **33**, 423–4.
742. Acid-base equilibria in glacial acetic acid: III. Acidity scale. Potentiometric determination of dissociation constants of acids, bases and salts (With S. Bruckenstein). *J. Amer. Chem. Soc.*, 1956, **78**, 2974.
743. The reaction between aquo ferrous iron and cumene hydroperoxide (With W. L. Reynolds). *J. Phys. Chem.*, 1956, **60**, 969.
744. The reactions of ferrous versenate and ferrous pyrophosphate with cumene hydroperoxide (W. L. Reynolds). *Ibid.*, 1956, **60**, 996.
745. Amperometric titrations. *J. Assoc, Offic. Agric. Chemists*, 1956, **39**, 47–9.
746. A redox system utilizing *N*-nitroso-acetanilide for the emulsion polymerization of styrene and of butadiene-styrene (With D. S. Brackman and E. J. Meehan). *J. Polymer Sci.*, 1956, **21**, 519–34.
747. Interpretation of acid-base titrations in glacial acetic acid, *Experientia*, supplementum V/3 1956, 33–45. Birhäuser Verlag, Basel.
748. Reduction of hexavalent chromium at the rotated platinum electrode. Permeability of the film formed (With A. M. Shams El Din). *J. Phys. Chem.*, 1956, **60**, 1564–8.
749. Acid-base equilibria in glacial acetic acid: IV. Quantitative interpretation of acid-base titrations in glacial acetic acid (With S. Bruckenstein). *J. Amer. Chem. Soc.*, 1957, **79**, 1–7.
750. Kinetics of the reaction between chromate and arsenic trioxide in alkaline medium. Induced reduction of oxygen by this couple (With M. A. Fineman). *J. Phys. Chem.*, 1956, **60**, 1383–88.

751. Polarography in acetonitrile: I. Metal ions which have comparable polarographic properties in acetonitrile and in water (With J. F. Coetzee). *J. Amer. Chem. Soc.*, 1957, **79,** 870–74.
752. Polarography in acetonitrile: II. Metal ions which have significantly different polarographic properties in acetonitrile and in water. Anodic waves. Voltammetry at rotated platinum electrode (With J. F. Coetzee). *Ibid.*, 1957, **79,** 1852–58.
753. Mechanism of retardation in emulsion polymerization of styrene (With E. J. Meehan, Nora Tamberg and C. L. Segal). *J. Polymer Sci.*, 1957, **26,** 215–32.
754. Voltammetry and amperometric titration at the rotated platinum electrode of manganese (II), (III), and (VII) in pyrophosphate medium (With Einar Jacobsen). *Microchem. J.*, 1957, **1,** 3–16.
755. A stable equimolar copper(II)-albumin complex (With B. R. Willeford, Jr). *J. Amer. Chem. Soc.*, 1957, **79,** 2656–57.
756. Equations for the limiting current at the rotated dropping mercury electrode (With Y. Okinaka). *Ibid.*, 1957, **79,** 3326–39.
757. The composition and formation of cobalt complexes with 1-nitroso-2-naphthol (With Einar Jacobsen). *Ibid.*, 1957, **79,** 3677–81.
758. The use of cacotheline as an oxidation-reduction indicator for the volumetric oxidation of iron (With D. N. Hume). *Analyt. Chim. Acta*, 1957, **16,** 415–18.
759. Voltammetric behavior of the iron(II)-(III) and cerium(III)-(IV) couples in potentiometric titrations at constant current and amperometric titrations with two indicator electrodes (With E. R. Nightingale, Jr.). *Ibid.*, 1957, **17,** 329–38.
760. The amperometric titration of bovine serum albumin with copper^{II} (With Bennett R. Willeford). *J. Amer. Chem. Soc.*, 1957, **79,** 2656.
761. Reactivity of sulfhydryl and disulfide upon denaturation of proteins (With Ada Anastasi, B. H. Tan and G. S. Deshmukh). *J. Amer. Chem. Soc.*, 1957, **79,** 5102.
762. Polarography in acetonitrile: III (With J. F. Coetzee). *Ibid.*, 1957, **79,** 6110.
763. Acid base equilibria in glacial acetic acid: V. The effect of water on potentiometric and indicator end-points in acid-base titrations in acetic acid (With S. Bruckenstein). *Ibid.*, 1957, **79,** 5915.
764. Application of the rotated dropping mercury electrode to the analysis of mixtures of electroactive substances (With Y. Okinaka and T. Fujinaga). *Analyt. Chim. Acta*, 1958, **18,** 295.
765. Factors to be considered in quantitative polarography with the rotated dropping mercury electrode (With Y. Okinaka). *Ibid.*, 1958, **18,** 83.
766. Mechanism of retardation in emulsion polymerization of styrene (With E. J. Meehan, Nora Tamberg and C. L. Segal). *J. Polymer Sci.*, 1957, **24,** 215–32.
767. Voltammetric behavior of the iron (II)-(III) and cerium (III)-(IV) couples in potentiometric titrations at constant current and amperometric titrations with two indicator electrodes (With E. R. Nightingale, Jr.). *Analyt. Chim. Acta.*, 1957, **17,** 329–38.
768. Reactivity of sulfhydryl and disulfide in proteins, II. Reactive disulfide as related to viscosity and potical rotation in denatured bovine serum albumin (With Ada Anastasi and B. H. Tan). *J. Amer. Chem. Soc.*, 1958, **80,** 3235–40.

769. Reactivity of sulfhydryl and disulfide in proteins: III. Oxidation with ferricyanide of sulfhydryl in native and denatured bovine serum albumin (With Ada Anastasi). *Ibid.*, 1958, **80,** 4248–50.
770. Controlled current polarography at the dropping-mercury electrode (With Y. Okinaka). *Ibid.*, 1958, **80,** 4452–58.
771. Utilization of radioactive isotopes in the study of aging of crystalline precipitates. *Trudy Kom. analit. Khim., Akad. Nauk. U.S.S.R. Inst. Geokhim. i, Anal. Khim.*, 1958, **9,** 98–114.
772. Polarography of sodium hydrosulfate and sodium formaldehyde sulfoxylate at the dropping mercury electrode (With N. Tamberg). *J. Polarog. Soc.*, 1958, **3,** 54–63.
773. Potentiometric titrations with an attackable electrode. The bimetallic electrode pair platinum-tungsten (With E. R. Nightingale, Jr). *Analyt. Chim. Acta*, 1958, **19,** 593–600.
774. Amperometric determination of fluoride at a rotated aluminum electrode (With C. J. Sambucetti). *J. Amer. Chem. Soc.*, 1959, **81,** 1516–17.
775. Reactivity of sulfhydryl and disulfide in proteins: IV. Reaction between disulfide and sulfite in bovine serum albumin denatured in guanidine hydrochloride and urea solutions (With Ada Anastasi and B. H. Tan). *Ibid.*, 1959, **81,** 2047–52.
776. The induced reduction at the dropping mercury electrode of colloidal silver bromide by dicyano argentate (I) ion (With R. C. Bowers). *Ibid.*, 1959, **81,** 1836–40.
777. Effect of surface-active substances on polarographic waves of copper^{II} ions (With Y. Okanaka). *Ibid.*, 1959, **81,** 2296–2302.
778. Voltammetric, potentiometric, and amperometric studies with a rotated aluminum wire electrode: I. Voltammetric behavior of the rotated aluminum electrode (With C. J. Sambucetti). *Analyt. Chim. Acta*, 1959, **21,** 17–24.
779. II. The rotated aluminum electrode as indicator electrode in potentiometric and amperometric acid-base titrations. *Ibid.*, 1959, **21,** 155–65.
780. Formation and aging of precipitates: XLVI. Precipitation of lead sulfate at room temperatures (With B. van't Riek). *J. Phys. Chem.*, 1959, **63,** 817–23.
781. Voltammetric, potentiometric and amperometric studies with a rotated aluminum wire electrode: III. Amperometric determination of fluoride with the rotated aluminum electrode (With C. J. Sambucetti). *Analyt. Chim. Acta*, 1959, **21,** 233–45.
782. Amperometric titration of albumin in blood serum by copper^{II} (With B. R. Willeford, Jr. and D. Singh). *Ibid.*, 1960, **22,** 92–5.
783. Redox recipes: X. Recipe with ferric versenate, sodium dithionite, and hydroperoxide as activating system. (Veroxathionite recipe) (With E. J. Meehan.) *J. Appl. Polymer Sci.*, 1959, **1,** 200–11.
784. Mechanism of oxidation of hydrazine by ferric ethylenediaminetetra-acetate (FeY^{-}) (With H. Minato, E. J. Meehan and C. Auerbach). *J. Amer. Chem. Soc.*, 1959, **81,** 6168–73.
785. Determination of traces of hydroperoxide by reaction with arsenic (III). Application to determination in polymer latex. (With E. J. Meehan, S. Bruckenstein and H. Minato) *Microchem. J.*, 1960, **4,** 33–41.

786. Characteristics of irreversible waves and kinetic currents at the rotated dropping mercury electrode (With Y. Okinaka). *J. Amer. Chem. Soc.*, 1960, **82,** 324–9.

787–788. Voltammetric, potentiometric and amperometric studies with a rotated aluminum wire electrode: IV. A comparison of the Baker and Morrison cell with a rotated aluminum electrode (With C. J. Sambucetti). *Analyt. Chim. Acta.*, 1960, **22,** 253-60.
V. Amperometric titration of fluoride with aluminum (With E. J. Meehan and C. J. Sambucetti). *Ibid.*, 351–63.

789. The interaction of copper^{II} with bovine serum albumin (With B. R. Willeford, Jr.). *J. Amer. Chem. Soc.*, 1960, **80,** 5673–8.

790. Polarography of copper^{II} thiocyanate solutions (With Y. Okinaka). *Rec. Trav. chim.*, 1960, **79,** 551–6.

791. Post adsorption wave of cuprous thiocyanate in polarograms of dilute thiocyanate solutions containing copper^{II} (With Y. Okinaka). *J. Amer. Chem. Soc.*, 1960, **82,** 3528–33.

792. Reactivity of sulfhydryl and disulfide in proteins: V. Reversal of denaturation of bovine serum albumin in 4*M* guanidine hydrochloride of 8*M* urea and of splitting of disulfide groups in 4*M* guanidine hydrochloride (With Ada Anastasi and B. H. Tan). *J. Amer. Chem. Soc.*, 1960, **82,** 4147–51.

793. Formation and aging of precipitates: XLVII. Maxima in particle size of lead sulfate formed under various conditions (With B. Van't Riet). *J. Phys. Chem.*, 1960, **64,** 1045–7.

794. Amperometric cerimetric titration of iron^{II} with ferroïn as indicator (With B. B. Bhayie). *Microchem. J.*, 1960, **4,** 451–7.

795. Amperometric argentimetric and mercurimetric titration of sulfhydryl (groups): I. Argentimetric titration (With J. Eisenstadter). *Analyt. Chim. Acta*, 1961, **24,** 80–83.

796. Effects on polarographic waves of the formation of insoluble films on dropping mercury (With Y. Okinaka). *J. Amer. Chem. Soc.*, 1961, **83,** 47–53.

797. Amperometric argentimetric and mercurimetric titration of sulfhydryl (groups): II. Mercurimetric titration (With J. Eisenstadter). *Analyt. Chim. Acta.*, 1961, **24,** 280–93.

798. Polarographic and acid properties of thorium perchlorate in acetonitrile (With S. Ikeda). *J. Phys. Chem.*, 1961, **65,** 1020–6.

799. Reaction of cumene hydroperoxide with hydrazine induced by the reaction between iron^{III} EDTA and hydrazine (With E. J. Meehan, C. Auerbach, and H. Minato). *J. Amer. Chem. Soc.*, 1961, **83,** 2232–4,

800. Polarography and voltammetry in dimethyl sulfoxide (With T. B. Reddy). *J. Electrochem. Soc.*, 1961, **108,** 980–5.

801. Acid-base equilibriums in acetonitrile (With S. Bruckenstein and M. K. Chantooni, Jr.). *J. Amer. Chem. Soc.*, 1961, **83,** 3927–35.

802. Recent modifications of the Heyrovský dropping mercury electrode (With Y. Okinaka). *Progr. Polarog.*, 1962, **2,** 257–81.

803. *N*-Methylacetamide as polarographic solvent (With L. A. Knecht). *Inorg. Chem.*, 1962, **1,** 195–203.

804. Acid-base strength in dimethyl sulfoxide (With T. B. Reddy). *Ibid.*, 1962, **1,** 189–74.

805. Oxidation of n-octylmercaptan by ferricyanide in acetone-water solution (With E. J. Meehan, M. S. Tsao and Q. W. Choi). *J. Phys. Chem.*, 1962, **66**, 1233–7.
806. Reaction between ferricyanide and 2-mercaptoethanol (With E. J. Meehan and H. Kakiuchi). *Ibid.*, 1962, **66**, 1238–41.
807. The stability constant of the $H_2SO_4HSO_4^-$ ion and its mobility in acetonitrile (With M. K. Chantooni, Jr.). *Ibid.*, 1962, **66**, 1675–78.
808. The effect of cell resistance on acute polarographic maxima (With J. C. Marshall and S. L. Gupta). *J. Electroanalyt. Chem.*, 1962, **3**, 209.
809. Polarography of molybdenum^{VI} in aqueous sulfuric acid solutions (With I. Hodara). *Ibid.*, 1962, **4**, 369.
810. Polarographic study of the molybdenum catalysed reduction of chlorate, perchlorate and nitrate (With I. Hodara). *J. Electroanalyt. Chem.*, 1963, **5**, 2.
811. Effect of tungsten^{VI} on molybdenum^{VI}-catalysed reduction waves of chlorate, nitrate and perchlorate (With I. Hodara). *Ibid.*, 1963, **5**, 165.
812. The composition and reactivity of the precipitate formed at the dropping mercury electrode upon one-electron reduction of hexa-amminecobalt(III) (with S. E. Khalafalla). *Inorg. Chem.*, 1963, **2**, 133.
813. Calculated and experimental conductometric titration curves of intermediately strong acids and bases in acetonitrile (With M. K. Chantooni, Jr.). *J. Amer. Chem. Soc.*, 1963, **85**, 426.
814. Education of chemists in the U.S.S.R. *Analyt. Chem.*, 1963, **35**, 41A.
815. Effect of iodide and bromide on the one-electron polarographic reduction of hexa-amminecobalt(III) chloride (With S. E. Khalafalla). *J. Amer. Chem. Soc.*, 1963, **85**, 664.
816. Effect of polarograms of the product formed in the one-electron reduction of hexa-amminecobalt(III) ion (With S. E. Khalafalla). *Rev. Polarog. (Japan)*, 1963, **11**, 11.
817. Arsenic^{IV} as an intermediate in the induced oxidation of arsenic^{III} by the iron^{II}-persulphate reaction and the photoreduction of iron^{III}—I: Absence of oxygen (With R. Woods and E. J. Meehan). *J. Amer. Chem. Soc.*, 1963, **85**, 2385.
818. Effect of heteroconjugation on acid-base conductometric titration curves of 3,5-dinitrobenzoic acid in acetonitrile (With M. K. Chantooni, Jr.). *Ibid.*, 1963, **85**, 2195.
819. Arsenic^{IV} as an intermediate in the induced oxidation of arsenic^{III} by the iron^{II}-persulphate reaction and the photoreduction of iron^{III}—II: Presence of oxygen (With R. Woods and E. J. Meehan). *Ibid.*, 1963, **85**, 3334.
820. The ratio of the first to the second diffusion current of oxygen at the dropping mercury electrode: Diffusion coefficient of oxygen (With K. Izutsu). *Ibid.*, 1964, in press.
821. Exaltation of the first oxygen wave at the dropping mercury electrode (With K. Izutsu). *J. Electroanalyt. Chem.*, 1964, in press.
822. Arsenic^{IV} as an intermediate in the induced oxidation of arsenic^{III} by the iron^{II}-hydrogen peroxide reaction (With R. Woods and E. J. Meehan). *J. Phys. Chem.*, 1964, in press.
823. Polarography in acetonitrile of titanium tetrachloride and tetra-iodide in various supporting electrolytes (With F. G. Thomas). *Inorg. Chem.*, 1964, in press.

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NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

FEDERAL GERMAN REPUBLIC

Friday–Saturday 19–27 *June* 1964: **European Convention of Chemical Engineering 1964:** Frankfurt am Main.

This will include the **1964 ACHEMA Congress,** of which the following parts of the programme may be of interest to analytical chemists:

Friday, 19 *June: Measurement and measured-value transformation in chemical technology*

Intermittierende elektrochemische Sauerstoffmessungen in verungreinigten Gewässern.	F. Tödt
Neue elektrochemische Meßanordnungen zur Kontrole von Spurenkonzentrationen reduzierender Stoffe in Gasen und Flüssigkeiten.	G. Teske
Volltransistorisierter Gleichspannungsverstärker für pH-Messungen.	P. Wunderer
Durchflußmessung von aggressiven und mit Festoffen versetzten Flüssigkeiten.	H. Engelhardt
Ein neuer Meßplatz zur Bestimmung der Stoffkonstanten E_T und tan δ von Proben mit weitgehend beliebigen Formen bei 3000 *MHz.*	G. Schilling
Emploi du chromatographe automatique à l'usine de Lacq.	R. Caboz
Die Flammenionisation zur kontinuierlichen Bestimmung von Qualitätsgrößen.	G. Steinmüller

Saturday, 20 *June*

Szintillationsspektrometrie von α und β-Strahlung mit Cäsiumjodid.	K. H. König
Neuere Entwicklung bei der Meßwertgebung mit Radioisotopen.	A. Trost
Isotopenanwendung in der chemischen Industrie.	K. Czeija
Kontinuierliche Dichtemessung in Industriebetrieben.	H. Krech
Überwachung der Äthylenproduktion mit dem Massenspektrometer.	H. G. Lossau
The infrared analyser—a powerful analytical tool for on-line chemical analysis.	E. G. Meyer
Neue Erfahrungen bei der kontinuierlichen Überwachung der Viskosität.	H. Kühlewein

Tuesday, 23 *June: New physical methods of chemical analysis, especially methods of trace analysis*

Brennstoffzellen als Spurenmeßgeräte.	P. Hersch
Fortschritte in der Entwicklung der Analyse mit Hochfrequenz.	K. Cruse
Impurity analysis in high polymers by the pulse dielectric method.	P. Hedvig
Ein neues Gerät für Elektronenbeugung im Ultravakuum.	M. Gribi und L. Wegmann
Neuere Entwicklungstendenzen in der EPR-Spektrometrie.	H. G. Thom
Ein Universalgerät für Kernresonanzuntersuchungen.	F. Furrer
High precision comparative polarography.	H. M. Davis
Some analytical applications of differential cathode ray polarography.	R. C. Rooney
Coulo-Halometrie mit galvanischen Zellen.	P. Hersch

Wednesday, 24 *June*

Dreidimensionale Dünnschicht-Chromatographie bei tieferen Temperaturen.	E. Stahl
New developments in column technology in gas chromatography.	L. S. Ettre

Arbeitsmethoden der Gaschromatographie.	E. Rödel
Erfahrungen auf dem Gebiet der gaschromatographischen Spurenanalyse mit neuen hochempfindlichen Detektoren.	E. Thom
Separation of multicomponent mixtures by continuous gas-liquid chromatography.	P. E. Barker
Applications of duel channel gas chromatography.	J. Amy, K. P. Dimick and T. Z. Chu
Thermische Fragmentierung und Strukturbestimmung organischer Verbindungen.	W. Simon
Versuche zur Spurenanalyse von Kohlenwasserstoffgasen.	M. Freund, L. Szepesy und F. Simon
Die Anwendung der Gas-Chromatographie in der CHN-Analyse.	K. Derge

Thursday, 25 *June*

Die Bedeutung einer Erweiterung des Spektralbereiches in der Infrarot-Spektroskopie.	G. Kemmner und F. Brunner
Automatisierte Röntgenfluoreszenz-Analyse.	H. Neff
Röntgenmikroanalyse elektronenmikroskopischer Präparate.	K.-H. Herrmann und H. Neff
Ölverschmutzung in Wasser und Gewässern. Nachweis und quantitative Bestimmung mit dem IR-Spektrophotometer.	W. Fastabend
Eine neue Apparatur zur Prüfung der Lichtund Wetterechtheit von Färbungen auf dem Textilgebeit, von Kunststoffen, Lackanstrichen und Gumm.	E. O. Seitz
Flammenspektrometrische Möglichkeiten zur Bestimmung von Phosphor in phosphororganischen Verbindungen.	W. Schmidt
Strahlenquellen für die atomare Absorptionsspektroskopie.	K. Osterhammel
A new instrument for analytical atomic absorption spectrophotometry.	W. J. Price
Eine neue Geräteserie selbstkompensierender Analysenautomaten für die Spurenmessung.	H. Fuhrmann
Kontinuierliches Meßverfahren zur Überwachung von MAK-Werten.	W. Gey und K. Schuster

Friday, 26 *June*

Submicro methods of organic analysis.	R. Belcher
Eine neue Vakuumthermowaage.	H. G. Wiedemann
Eine neue Dosierungsmethode zur Durchführung von Mikroreaktionen.	H. Straubel
Neue Verfahren auf dem Gebiet der thermometrischen Titration.	H. Knauer
Polymer molecular weight analysis by gel permeation chromatography.	L. E. Maley
Neue Anwendungsgebeite des Verfahrens der Gel-Filtration durch die Entwicklung neuer Dextrangele.	B. Gelotte
Die Endpunktbestimmung in der analytischen Chemie.	H. Jucker
Neue Laborwaagen mit Vorrichtungen zur Bedienungserleichterung.	H. Hartwig
Gravimetrische Sondergeräte für physikalischchemische Untersuchungen.	B. Kassner

The **Deutsches Atomforum e. V.** is organising for the first time a series of lectures within the framework of the Convention on 25 June, entitled *Nuclear Radiations in Science and Industry.* The following of the lectures may be of interest to analytical chemists:

Aktivierungsanalyse und Erzeugung kurzlebiger Isotope in Chemie und Technik in kleinen Reaktoren.	A. Thiel
Das kontinuierliche Beta-Gamma-Photometer als Hilfsmittel bei der Uberwachung und seine Grenzen.	K. H. Waechter
Sunnschichtmelzen mit radioaktiven Stoffen. Dünnschichtchromatographie mittels Radionukliden.	G. Boucke
Zonenschmelzen mit radioaktiven Stoffen.	H. Schildknecht
Bremsstrahlen-Fluoreszenzanalyse.	W. Kühn
Verweilzeit-Messungen mittels radioaktiver Indikatoren.	D. Schulz-Pillot

Further information can be obtained from DECHEMA, 6 Frankfurt (Main) 7, Postfach 7746, Bundesrepublik Deutschland.

FRANCE

La Commission Internationale d'Analyse "C.I.A." du **Comité Internationale de la Détergence** "C.I.D." a tenu sa 7ème session les 24 et 25 Octobre 1963 à Saint-Gall, sur invitation du Comité Suisse de la Détergence, sous la présidence du Prof. JACINI (Italie).

Après avoir entendu un rapport sur l'activité générale, depuis un an, du C.I.D. par son Secrétaire Général, M, DE WIT. et sur l'organisation du 4ème *Congres International de la Détergence* qui doit avoir lieu à Bruxelles du 7 au 12 Septembre 1964, les membres de la C.I.A. discutèrent les résultats des différentes analyses circulaires effectuées en 1963, concernant notamment:

—analyse des alkylsulfonates de sodium,
—analyse de mélanges d'alkylsulfates primaires et d'alkylarènesulfonates,
—analyse de mélanges de non-ioniques, d'alkylarènesulfonates et de savon,

toutes réalisées à l'aide de méthodes récemment mises au point par les pays appartenant à la Commission et basées sur l'emploi des échangeurs d'ions. Ces travaux seront repris au cours de l'année prochaine en vue de leur apporter certaines améliorations avant de les faire homolguer sur le plan international.

Les discussions sur l'analyse des non-ioniques ont occupé une grande partie de la session. L'étude de méthodes reproductibles a été confiée, il y a deux ans, à un Groupe de Travail, dont les travaux avancent rapidement puisqu'il a pu soumettre à ses collègues de la C.I.A., qui les ont acceptées, des propositions pour les déterminations titrimétriques et celles de l'eau et des cendres, qui seront presentées incessamment, pour homologation, à l'Organisation Internationale de Normalisation "I.S.O.".

Le programme futur de ce Groupe de Travail comprendra la poursuite des recherches sur la détermination de l'oxyde d'éthylène, de l'indice d'hydroxyle, des polyglycols libres, et des alkylphénols libres dans les alkylphénols oxyéthylènes. D'autres Commissions devant s'attacher plus particulièrement à la séparation des hydrocarbures non sulfonés et à la détermination des polyoxyéthyles sulfatés.

Il est à noter que les méthodes d'analyse déjà soumises a l'I.S.O. semblent devoir être adoptées sans difficulté par les membres de cette Organisation, ce qui est un grand encouragement pour la C.I.A.

POLAND

Tuesday–Saturday 15–19 *September* 1964: **XXXVth International Congress of Industrial Chemistry:** Varsovie.

Among the many sections of the Congress, one is devoted to *Analytical Chemistry.* Further information can be obtained from the Scientific Committee of the XXXVth International Congress of Industrial Chemistry, Warsaw 86, skr. poczt. 26, Poland.

UNITED KINGDOM

Wednesday 4 *March* 1964: **Annual General Meeting** followed by **Bernard Dyer Memorial Lecture:** *Society for Analytical Chemistry:* Burlington House, London W.1: 3.00 p.m.

Wednesday 11 *March* 1964: **Annual General Meeting** followed by **Analysis of Peroxygen Compounds:** C. WHALLEY: *Society for Analytical Chemistry, Midlands Section:* University, Edgbaston, Birmingham 15: 6.30 p.m.

Saturday 14 *March* 1964: **Biochemistry of Quinones:** R. A. MORTON: *Society for Analytical Chemistry, North of England Section:* City Laboratories, Mount Pleasant, Liverpool: 2.15 p.m.

Wednesday 18 *March* 1964: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group: The Feathers,* Tudor Street, London E.C.4: 6.30 p.m.

Friday 20 *March* 1964: **Organic Analytical Reagents—A Survey of Some New Work:** W. I. STEPHEN: *Society for Analytical Chemistry, Scottish Section:* Queen's College, Dundee: 7.15 p.m.

Tuesday 24 *March* 1964: **The Work of a Public Analyst:** R. A. DALLEY: *Society for Analytical Chemistry, Midlands Section:* Nottingham and District Technical College: 7.00 p.m.

Tuesday 24 *March* 1964: **Physical Methods Applied to Examination of Archaeological Remains:** E. T. HALL and A. E. A. WERNER: *Society for Analytical Chemistry, Physical Methods Group:* Burlington House, London W.1: 6.30 p.m.

Wednesday 14 *October* 1964: Symposium on **Thin-Layer Chromatography:** *Society for Analytical Chemistry, Thin-Layer Chromatography Panel* and *Midlands Section* with *Royal Institute of Chemistry, Birmingham and Midlands Section:* University, Edgbaston, Birmingham 15.

The programme will consist of a Plenary Lecture by Professor Dr. E. STAHL and the following lectures:

Thin-Layer Chromatography in Biosynthetic Studies.	T. W. GOODWIN
Recent Developments in Thin-Layer Chromatographic Equipment.	R. P. HIRSCH

Thin-layer Chromatography on Ion-Exchange Media.	C. S. KNIGHT
Thin-Layer Chromatography in Clinical Chemistry.	J. G. LINES
Exploitation of Thin-Layer Chromatography in Plant Chemistry.	E. J. SHELLARD

Further information can be obtained from Mr. M. L. RICHARDSON, John and E. Sturge, Lifford Lane, Kings Norton, Birmingham 30.

At the **First Annual General Meeting** of the *Atomic Absorption Spectroscopy Discussion Panel* of the *Physical Methods Group* of the *Society for Analytical Chemistry*, held on Tuesday, 3 December, 1963, the following Officers were elected for the forthcoming year:—

Chairman: W. T. ELWELL
Secretary: D. MOORE, 98 St. Pancras Way, Camden Road, London N.W.1.

British Standards Institution has announced the following *New British Standards*:—

B.S. 2649: *Methods for the analysis of glass: Part* 4: 1963: *Recommended procedure for the analysis of fluoride-opal glasses.* This recommends detailed analytical procedures for determining all of the important constituents of the so-called 'fluoride-opal' glasses based on investigations carried out by the Society of Glass Technology. (*Price* 6s.)

B.S. 3406: *Methods for the determination of particle size of powders: Part* 2: 1963: *Liquid sedimentation methods.* This describes methods of determination of the size distribution of particles in those fractions of powders which pass a 75 μ British Standard test sieve, using the principle of liquid sedimentation. Four methods are described, *viz.* the fixed depth pipette, the fixed position pipette, the liquid column method with sedimentation accumulation and the liquid column method with sediment extraction. The basic principle (Stokes's law) is described in the foreward. An appendix advises on liquid suspended media and dispersing agents, providing a list of suitable suspended media for many materials. Other appendices describe methods of evaluating a size analysis instrument and the correlation of results from different methods of size determination. (*Price* 15s.)

Part 4: *Optical microscope method.* This describes a method of determination of the size distribution of particles in those fractions of powders which pass through a 75 μ British Standard test sieve. A representative sample of powder to be sized is dispersed and placed on a glass slide and the particles are viewed through a microscope by means of transmitted light. The areas of the magnified images of the particles are compared with the areas of reference circles of known size inscribed on a graticule and simultaneously visible. The relative numbers of particles in each of a series of size classes are determined. These numbers, expressed as percentages, constitute the size distribution by number. From the relative numbers in the size classes it is possible to calculate the size distribution by weight, provided it is assumed that particles of all sizes have the same shape in the sense that the square root of the projected area of a particle stands in a constant ratio to the cube root of the volume of the particle, and that all of the particles have the same density. (*Price* 20s.)

B.S. 3681: 1963: *Methods for the sampling and testing of lightweight aggregates for concrete.* This describes methods for sampling and testing of lightweight aggregates for concrete. The tests cover bulk density, sieve analysis, apparent specific gravity, sulphate content, volatile matter, loss-on-ignition, carbon content and soundness. (*Price* 7s. 6d.)

The following *Revised British Standards* have also been announced:—

B.S. 1428: *Microchemical apparatus: Part* 11: 1963: *Combustion boats and sheath for microchemical analysis.* This specifies the following apparatus designed to fit the microcombustion tubes specified in other parts of B.S. 1428: one size of platinum combustion boat and a sheath to fit it and three sizes of porcelain combustion boat. It includes dimensional drawings as well as appropriate requirements for material, weight and marking, and for constancy of weight of the platinum boat or sheath or ignition. It also gives desirable limits for constancy of weight of porcelain boats on ignition or heating with acid, but these are not a mandatory part of the specification. (*Price* 4s. 6d.)

B.S. 1747: *Methods for the measurement of air pollution: Part* 4: 1963: *The lead dioxide method.* This covers the construction and use of apparatus for the lead dioxide method of measuring the reactivity of atmospheric sulphur compounds. (*Price* 5s.)

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 14: 1963: *Analysis of coal ash and coke ash.* This deals with the determination by chemical analysis of the major constituents in samples of coal ash or coke ash. An appendix describes a spectrographic method by which certain constituents can be determined speedily and with sufficient precision for most purposes. (*Price* 10s.)

B.S. 1715: 1963: *Methods of analysis of soaps and soap powders.* This describes methods of sampling and the preparation of the sample for analysis, and the following determinations: total fatty matter, alkali combined as soap, total alkali, titre, matter insoluble in ethanol, matter insoluble in water, free alkali, free fatty acids, unsaponifiable matter and unsaponified fat, chlorides, silica, phosphate, per-salts, rosin, glycerol, loss on drying at 100–105° and water. (*Price* 16s.)

B.S. 1756: *Methods for the sampling and analysis of flue gases. Part* 5: 1963: *Semi-routine analyses.* This describes semi-routine methods for the determination of carbon dioxide, carbon monoxide and total oxides of sulphur, mainly employed for the assessment of the combustion performance of domestic gas appliances. (*Price* 6s.)

UNITED STATES OF AMERICA

Monday–Friday 2–6 *March* 1964: **15th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *Analytical Chemistry Group, Pittsburgh Section ACS and Spectroscopy Society of Pittsburgh:* Penn-Sheraton Hotel, Pittsburgh, Pa.

The programme is as follows:—

Monday, 2 *March: Morning*

Gas Chromatography—Detectors

Characteristics of a sensitive and absolute ultrasonic detector for gas chromatography.	F. W. Noble and K. Abel
Response of hotwire thermal conductivity cell.	D. W. Robinson and D. M. Rosie
Electron drift-velocity detector for gas chromatography.	V. N. Smith and J. F. Fidiam
Piezoelectric sorption detector.	W. H. King, Jr.
A high temperature hydrogen flame ionisation detector: A critical evaluation of design and operating characteristics.	A. C. Seibel
A rapid-scan far UV spectrophotometer for monitoring gas chromatograph effluent.	W. Kaye and F. Waska
A preliminary study of the characteristics of a photoionisation detector for gas chromatography.	J. F. Roesler

Instruments for Analysis

A fully automated analytical balance.	L. Cahn and H. Schultz
A versatile sorption hygrometer.	J. Kertzman
Electrodeless conductance measurements.	D. E. Burge and T. A. Olson
Galvanic determination of strong acids.	P. Hersch and C. Sambucett
Electronic potentiometer defines new standard in pH instrumentation	D. C. Douglass and E. F. Blondfield
A convenient solution calorimeter.	E. M. Arnett, J. J. Burke and L. V. Guild
Oxygen gauge.	W. M. Hickam
Instrument cloud point determinations.	J. L. Williams and N. Stein

Symposium on High Resolution NMR of Oriented Molecules

NMR in liquid crystals: PMR spectrum of benzene in a nematic solution.	A. Saupe
PMR investigations on oriented molecules.	G. Englert
Some studies of ordered nematic phases from highly resolved dipole-dipole splittings.	W. D. Phillips, J. C. Rowell and L. R. Melby
NMR spectra in single crystals.	P. C. Lauterbur

Monday, 2 *March: Afternoon*

Gas Chromatography—General

GLC studies of bile acid esters.	L. I. Braddock, J. J. Kelly and L. V. Hook
Analyses of chloraniline isomers by gas chromatography.	K. J. Bombaugh
Gas chromatography of water in hygroscopic liquids.	S. Ahuja, G. D. Chase and J. G. Nikelly
Analysis of diluted auto exhaust with a multi-columned gas chromatograph.	T. A. Bellar, M. L. Bellar and E. Sigsby, Jr.
Use of polymers as liquid phase in gas chromatographic analysis of high boiling-point compounds.	P. Shapras and G. C. Claver
Behaviour of phosphate pesticides in electron affinity detectors.	G. E. Cook, C. W. Stanley and J. E. Barney II

A microvapour-phase hydrogenation accessory for gas chromatographic analysis of glyceride oils.	T. L. Mounts and H. J. Dutton
Correlations between electron capturing ability and structure.	W. E. Baitinger and J. W. Amy

Spectrophotometric Methods of Analysis

Determination of microgram quantities of non-radioactive caesium in uranium and its compounds.	L. Silverman and R. S. Dunn
Determination of phosphorus in alloy steels.	G. A. Bauer
Automated procedures for spectrophotometric determination of silicon, phosphorus and manganese in steel.	P. H. Scholes and C. Thulbourne
Spectrophotometric determination of antimony in gold.	B. Yurash
Simultaneous spectrophotometric determination of calcium and magnesium with chlorophosphonazo III.	J. W. Ferguson, J. J. Richard J. W. O'Laughlin and C. V. Banks
Use of the molybdenum blue reaction in spectrophotometric determination of thallium.	L. Hargis and D. F. Boltz
An improved chloanilate method for determination of boron.	D. R. Peterson and J. R. Hayes
Precision analysis of highly pure bismuth telluride by differential spectrophotometry.	A. Eldridge, R. S. Kelly and R. Bastian
Indirect UV spectrophotometric determination of ammonia.	J. Howell and D. F. Boltz
New technique for study of photometric precision.	D. C. Nelson and R. C. Hawes
A study of a new spectrophotometric data acquisition system.	R. N. Rand and B. Helm

Symposium on High Resolution NMR of Oriented Molecules

NMR of polar molecules in an external electric field.	J. S. Waugh and J. D. Macomber
High resolution NMR spectra of molecules in an applied electric field.	K. A. McLauchlan

NMR and ESR Spectroscopy

Conformation of sugars and glucose polymers by PMR.	C. A. Glass
A nuclear resonance study of equilibria in the system boron trifluoride-methanol.	S. Brownstein
NMR study of isomeric pentadienes.	P. W. Flanagan and H. F. Smith
*Proton and carbon-*13 *NMR of coal derivatives and other carbonaceous materials.*	H. L. Retcofsky and R. A. Friedel
End-group analysis and number average MW determination of some polyalkylene glycols and their esters using NMR spectroscopy.	T. F. Page, Jr. and W. E. Bresler
A new type of spectrometer.	M. Takeuchi and T. Miyamae
ESR observations of oxidation-reduction process in some viscera.	T. Okabe and P. Y. Sakagishi

Tuesday, 3 *March: Morning*

Analysis of Inserstitial Elements in Metals

Co-operative testing programmes on gases in metals.	T. D. McKinley
Separation and identification of impurities in hydrided uranium-zirconium alloy.	L. Silverman and D. J. Klein
Rapid determination of nitrogen in refractory borides and nitrides.	J. W. Tereshko
Simultaneous determination of oxygen and nitrogen in refractory metals by d.c. carbon arc-gas chromatographic technique.	R. K. Winge and V. A. Fassel
Rapid determination of low concentrations of oxygen in potassium and NaK by a modified amalgamation technique.	G. Goldberg
Determination of carbon and carbon compounds in alkali metals.	J. C. Gerken, S. J. Rodgers and J. W. Mausteller
Rapid method for determination of micro amounts of sulphur in selenium.	L. Acs and S. Barabas
A recording linear-response gauge for vacuum fusion analysis.	H. F. Waldron

Liquid and Gas Chromatography

Improved techniques in liquid column chromatography.	L. E. Maley and J. L. Waters
Advantages and limitations of gel permeation chromatography.	L. E. Maley, G. E. Stackhouse and J. L. Waters
Thin-layer chromatography of organic phosphorus compounds.	C. W. Stanley
Quantitative analysis of mixtures separated on thin-layer chromatographic plates.	R. D. Spencer and B. H. Beggs
A method for recording elution curves on liquid column chromatography.	T. Naono
Effect of column shape on efficiency in gas chromatography preparative separations.	E. M. Taft, J. E. Booker and K. P. Dimick
Effect of injection port temperature on peak broadening in gas chromatography.	T. Haruki, T. Morij and K. Sato
Injection and vapourisation of samples in gas chromatography.	T. Johns and B. Thompson
Polymer analysis by pyrolysis-gas chromatography.	B. Groten

Polarography and Coulometric Analysis

A versatile polarographic analyser incorporating facilities for conventional d.c., rapid d.c., anodic stripping and a.c. polarography.	R. Kopp
Polarographic determination of mercury, tellurium and cadmium in HgTe and CdTe alloys.	M. C. Gardels and J. C. Cornwell
Polarographic determination of cadmium in stainless steel.	H. S. Karp and G. Krapf
Dissolved oxygen measurement by constant-potential continuous coulometry.	E. L. Eckfeldt and E. W. Shaffer
Chromatographic separation and coulometric determination of magnesium, calcium and strontium.	J. W. O'Laughlin, G. J. Kamin and C. V. Banks
Controlled potential coulometric studies of oxidation state ratios of trace elements.	B. W. Conroy and O. Menis
Application of controlled-potential coulometry to study of redox reactions in solution: The iridium^{III} chlorate system.	J. McClure and G. A. Rechnitz
A continuous automatic coulometric titrator.	P. Johnson, J. K. Jacobsen and R. J. Drago
An advanced automatic microcoulometer for trace sulphur and halogen analysis.	J. A. McNulty and A. R. Myers

Tuesday, 3 *March: Afternoon*

Symposium on Analysis of Gases and Non-Metallic Inclusions in Metals

Basic concepts of quantitative separation of alloy phases.	W. Koch
Neutron-activation analysis of metals for nitrogen, oxygen, silicon, phosphorus and sulphur.	V. P. Guinn
Analysis for non-metallic elements in metals by vacuum spark mass spectrography.	W. M. Henry and E. Blosser
Separation of oxide inclusions and nitrides.	W. Koch

Gas Chromatography—General

An ultra pure hydrogen generator for gas chromatography.	J. K. Jacobsen
Construction and performance of an IR chromatographic fraction analyser.	R. Brown and P. A. Wilks, Jr.
Design and performance of a portable ionisation chromatograph.	B. H. Andreen and D. V. Kniebes
Design considerations for an over-all high performance gas chromatograph.	M. R. Burnell
Pyrolysis gas chromatography with programmed temperature and capillary columns.	E. W. Cieplinski and L. S. Ettre
A continuous extractor for analysis of trace gases in liquids.	H. L. Ashmead, B. D. Crouch and J. A. Schmit
Minimising the time for the chromatographic analysis of complex mixtures.	T. B. Rooney and W. Aznavourian

An analogue bleed line compensation system.	E. J. Levy, D. G. Paul and L. Mikkelson
Multiple column compensation in process gas chromatographs.	E. L. Szonntagh and T. A. Gray

General Analytical Methods

Radio-release determination of vanadium.	A. S. Gillespie, Jr. and H. G. Richter
Rapid radiochemical determination of americium^{III}.	M. H. Campbell
Determination of nickel by magnetic susceptibility.	J. F. Reed
A rapid and simple mass spectrometric procedure for detection and determination of boron.	K. F. Sporek and R. A. Duvall
Indirect determination of fluorides by EDTA titration of samarium.	H. F. Combs and E. L. Grove
Determination of ferrous oxide in ferrites.	K. L. Cheng
Analysis of vanadium-gallium alloys based on displacement of vanadium^{V} *from its EDTA complex.*	M. C. Gardels
Determination of silica in presence of phosphate and fluoride.	F. W. Czech, T. P. Hrycyshyn and R. J. Fuchs
Determination of nitrate plus nitrite with special reference to air pollution.	N. A. Huey, C. C. Golden and R. E. Boone
Precise method for assay of potassium iodate by comparison with (primary standard) arsenic trioxide.	S. M. Tuthill, R. S. Sprague and W. C. Stoecker
Very accurately defined gas mixtures for use as primary standards.	H. G. Guillaume and G. Kanter
Use of cylinder gas mixtures to check moisture analysis instruments.	H. G. Guillaume

Wednesday, 4 *March: Morning*

Symposium on Chemical Applications of Far Infrared Spectroscopy

Recent developments in far infrared spectroscopy.	R. C. Lord
Interferometrics spectrometers: Their use as a practical laboratory tool.	A. Maki, L. R. Blaine and R. Nelson
Far infrared interferometer for the region 20–1000 *micron.*	J. Tadayon and J. N. A. Ridyard
Torsional vibrations in the far infrared spectrum.	W. G. Fateley, R. K. Harris, F. A. Miller and R. E. Witkowski
Hydrogen bond studies in the far infrared.	R. J. Jacobsen and J. W. Brasch
On the lattice spectrum of HI.	D. W. Robinson
Some infrared absorption studies in the 350–100 cm^{-1} *region.*	F. F. Bentley, N. T. McDevitt and A. Rozek

Analysis of Organic and Biological Material

Polymer MW determination by high temperature vapour pressure osmometry.	J. P. Burger
Ion-exchange separation of acetamide from ammonium acetate and its determination.	P. King and J. R. Simmler
Polarographic determination of aldehydes and acetals in alcohols.	C. C. Budke, D. K. Banerjee and F. J. Miller
Polarographic determination of microgram amounts of selenium in biological material.	G. D. Christian and W. C. Purdy
Determination of dl *and meso dibromosuccinic acids in aqueous solutions.*	R. Annino and D. J. Manzo
A new spectrofluorophotometer and its application to determination of biological substances.	K. Iwai, S. Kazawa and T. Haruki
Determination of phenyl-β-naphthylamine in polyurethane.	D. W. Chambers, D. M. Knight and J. L. Myers
A study of the pi complexes of trinitrofluorenone: Determination of amines, phenols and aromatic hydrocarbons.	G. H. Schenk, P. Wines and C. Mojzis
A new automated apparatus for determination of oxygen in organic compounds.	M. E. Ebeling and D. W. Marcinkus

Thermal Analysis and Potentiometric Analysis

Differential thermal analysis using self-generated atmospheres at supra-ambient pressures.	P. D. Garn
Application of differential thermal analysis to quantitative analysis.	J. Justin and N. Brenner
A semi-micro thermogravimetric analyser.	R. W. Tabeling
Determination of fluosulphonic acid in solutions containing large amounts of hydrofluoric, sulphuric and fluosulphonic acids.	W. E. Skillmann and S. A. Ashworth
Differential potentiometric determination of palladium in presence of platinum.	S. Barabas and J. Vinaric
Comparison of methanol with water as solvent in potentiometric titration of halides.	H. T. Havacek and W. B. Swann

Symposium on Chemical Applications of Far Infrared Spectroscopy

The cooled germanium bolometer as a far infrared detector.	C. E. Jones, Jr., R. Hilton, J. B. Damrel, Jr., and C. C. Helms
A comparison of the Golay cell and the thermocouple as far infrared detectors.	G. L. Carlson
Far-infrared instrumentation: Second generation.	G. T. Keahl, H. J. Sloane and M. Lu
Special sampling system for far infrared.	A. J. Russo and E. H. Siegler, Jr.
Low frequency infrared spectrum and vibrational assignment of glyoxal.	R. K. Harris
Infrared absorption study of some metal oxides in the region 350 *to* 70 cm^{-1}.	N. T. McDevitt, W. L. Baun and F. F. Bentley
Far infrared spectra of DL-leucine and DL-2-methylleucine.	L. May and M. St. L. Eaton

Infrared Sampling and ATR

Arsenic trichloride as a solvent for NMR and IR spectroscopy.	H. Szymanski, A. Bluemle, D. Bakalik and J. LaFanora
Design and application of a high temperature IR gas cell.	R. W. Rinehart, G. E. Bronson and A. W. Crowley
Soldering non-metals to metals for construction of improved IR absorption cells.	J. S. Ard
New IR absorption cells for macro to ultramicro quantities, utilising soldered seals of windows to metals.	J. S. Ard
Microsampling techniques in the IR.	R. C. Gore
ATR and specular reflectance measurements in the IR.	D. E. McCarthy
Evaluation of some factors affecting reproducibility of ATR spectra.	R. L. Harris
Analysis of suspended particulates with membrane filters and ATR.	R. W. Hannah and J. L. Dwyer
ATR analysis of the non-volatile vehicle in unseparated paint.	R. J. McGowan

Apparatus and Equipment for X-Ray Spectrographic Analysis

Effects of X-ray tube parameters on fluoresence analysis.	H. T. Dryer
Effect of excitation on X-ray emission intensities.	F. Bernstein
Description of an automatic "twin path" X-ray fluorescent spectrometer and its applications to process control.	C. C. Pyne
Multilayer soap films as analysing crystals in X-ray spectrometry.	A. J. Mabis and K. T. Knapp
Components for X-fluorescence spectroscopy in the 5–65 Å *wavelength region.*	J. A. Dunne
X-radiation analysers: Some advantages and disadvantages of various operating techniques.	R. Torkildsen
Automatic analysis of X-ray spectrographic data.	R. W. Deichert
A new simultaneous spectrometer for analysis of the light and heavy elements in static and dynamic samples.	J. F. Croke and W. J. Pfoser

Thursday, 5 March: Morning

Instrumentation for Molecular Spectroscopy

A new routine spectrophotometer.	J. J. J. Staunton and R. E. Boostrom
An across-the-counter double beam microscope spectrophotometer.	H. C. Duecker and E. R. Lippincott

Performance of the model 350 recording spectrophotometer in the far UV region.	T. J. Porro, H. T. Morse and E. S. Gillette
An improved method for measuring optical rotatory dispersion.	G. R. Thiel and D. C. Demoth
A precision recording absolute spectrofluorimeter.	G. K. Turner
Raman spectra of small solid samples including lattice vibrations.	D. C. Nelson and W. N. Mitchell
A near IR spectrophotometer for physical measurements.	R. C. Hawes, J. R. Eno and K. A. Wickersheim
Design development of a new filter-grating IR spectrophotometer.	C. W. Warren, A. E. Chapple and R. P. Bauman
Construction and performance of a frustrated multiple internal reflectance IR spectrophotometer.	P. A. Wilks, Jr.
Continuous IR instrumentation in packaging converting operations.	I. L. Brazier

Emission Spectroscopy—Excitation Techniques

New studies with gas-controlled arc sources.	M. Margoshes
The hollow cathode tube as a source for optical emission spectroscopy.	J. E. Paterson
A year of progress in laser excited spectroscopy.	F. Brech
Characteristics of the laser source for spectral excitation.	S. D. Rasberry, B. F. Scribner and M. Margoshes
The laser as a direct excitation source in analytical emission spectroscopy.	R. L. Rupp and R. Bastian
On the spectral excitation mechanism and properties of high frequency plasma-flames and d.c. plasma-jets.	J. van Calker and W. Tappe

Infrared

Vibrational spectra of hexafluoracetone.	C. V. Berney
Infrared and Raman spectrum of methyl isocyanate.	R. E. Witkowski and W. G. Fateley
Asymmetric rotor band contours.	S. C. Wait
Infrared stretching frequency of Si—F bond.	G. W. Miller, R. Gagne and J. Vanek
Infrared spectral studies of sulphones in the 2000–250 cm^{-1} *region.*	W. R. Feairheller, J. E. Katon and F. F. Bentley
Infrared spectra of organophosphate and organophosphorothioate pesticides.	L. Kahn and C. H. Wayman
Infrared studies of water of hydration in inorganic acetates.	S. E. Wiberley and K. J. Eisentraut
Infrared spectra of condensed thiophenes and their alkyl derivatives.	F. R. McDonald and G. L. Cook

Thursday, 5 March: Afternoon

Coblentz Memorial Symposium

Coblentz memorial lecture.	G. B. B. M. Sutherland
Development of vibrational spectroscopy of high polymers.	S. Krimm
Electronic spectra of polyatomic molecules.	D. A. Ramsay

Emission and Mass Spectroscopy—Instrumentation

Sensitivity and accuracy of analysis by spark source mass spectrometry.	J. S. Halliday, W. A. Wolstenholme and J. D. Waldron
Discussion of an interference spectrometer with resolution in excess of 10^6.	J. O. Crote and D. C. Damoth
The lazyprobe, a device for sampling large objects non-destructively for emission spectrochemical analysis.	A. Arrak, G. Chaplenko and D. O. Landon
A new visual spectroscope and its application to metal analyses.	Y. Tachibana and K. Kobayashi

Minimisation of spectral background influence and results of its automatic removal in direct reading instrumentation for stainless steels.	W. R. Kennedy
Multichannel spectrophotometer.	C. Iida, K. Fuwa and B. L. Vallee
Automatic readout system for a spectrometer.	H. R. Gram, Jr.

Atomic Absorption Spectroscopy

Simultaneous multi-channel analysis by atomic absorption spectroscopy.	A. Strasheim and L. R. P. Butler
Hollow cathode lamps for atomic absorption spectroscopy.	C. Sebens, D. C. Manning and W. Slavin
Relation between the Ca-resonance line profile of the hollow cathode lamp or flame and absorption intensity in atomic absorption.	K. Yasudo and S. Matsudaira
Determination of selenium and tellurium in copper by atomic absorption spectrophotometry.	S. Sprague, D. C. Manning and W. Slavin

Friday, 6 March: Morning

Symposium on Application and Instrumentation for Electron Probe Analysis

Application of electron probe to determination of concentration gradients and dispersed phase compositions.	D. M. Koffman
Electron probe and metallographic characterisation of an NBS spectrometric low alloy steel standard.	R. E. Michaelis, H. Yakowitz and G. A. Moore
Recent advances in application and instrumentation of electron probe microanalysis.	D. A. Melford
Application of the Zeibold-Ogilvie empirical quantitative calculation method to electron beam microanalysis.	S. H. Moll
Quantitative microanalysis using the A.E.I. scanning electron probe microanalyser.	P. W. Wright
Progress in design of equipment for electron probe analysis.	E. Davidson, W. E. Fowler, H. Neuhaus and W. G. Shequen
On the backscattered electron image by silicon P-N junction through the electron probe X-ray microanalyser.	S. Kimoto and H. Hashimoto

Symposium on Spectra of Adsorbed Molecules

Application of ESR to study of heterogeneous catalysis.	R. J. Kokes
IR spectroscopy in study of adsorption at non-metallic surfaces.	R. S. McDonald
Application of IR spectroscopy to study of adsorption on metal surfaces.	J. W. Ward
Electronic spectra of adsorbed molecules.	H. P. Leftin
Hydrogen chemisorbed in silicon.	W. A. Pliskin

Emission Spectroscopy—Applications

Spectrographic determination of silicon, phosphorus and nickel in copper-germanium alloys.	A. M. Liebman, R. J. Carver, L. A. Tissot and J. R. Zuber
Quantitative analysis of major and minor constituents of silicate rocks and minerals by means of direct reading spectroscopy.	H. Schwander and J. B. Marling
Element calibrations by plasma jet solution spectrography.	E. H. Sirois
Methanol as a diluent for gas stabilised arc sources.	J. D. Nohe
Use of a nitrogen atmosphere to reduce matrix effects in analysis of aluminium alloys using point-to-plane spark excitation.	C. K. Matocha, J. Petit and W. H. Tingle
Spectrochemical determination of cobalt, nickel, aluminium and boron in commercial acid gold baths by solution technique.	E. F. McLain and W. H. Wade
A direct reading spectrochemical procedure for measurement of 19 minor elements in natural water.	J. F. Kopp and R. C. Kroner
Spectrochemical determination of microgram amounts of tantalum, niobium, titanium and hafnium in U_3O_8.	J. E. Scott and E. R. Shuster, Jr.
Multi-element spectrographic impurity analysis of graphite.	O. V. Coble and F. V. Fair

Friday 6 *March: Afternoon*

Electron Diffraction and Applied X-Ray Spectrography

A new high vacuum unit for electron diffraction combined with surface electron microscopy.	M. Gribi, L. Wegmann and L. M. Mountford
X-ray fluorescent determination of cobalt, zinc and iron in organic matrices.	S. A. Bartkiewicz and E. A. Hammatt
Internal standard X-ray spectrographic procedure for determination of calcium, barium, zinc and lead in hydrocarbons.	W. E. Burke, L. S. Hinds, G. E. Deodato, E. D. Sager, Jr. and R. E. Borup
X-ray spectrographic determination of trace thorium in U_3O_8.	J. E. Scott and E. R. Shuster, Jr.
X-ray emission analysis of solders by solution technique.	W. T. Barnes and D. E. Wilson
Combined X-ray spectrometric and IR method for determining sulphonate and sulphate concentration of detergent range alkylbenzene solutions.	S. D. Kullbom, W. K. Pollard and H. F. Smith
Digital programming applied to steel analysis.	P. Breckheimer and W. E. Fowler

Analyses by Microwave and Infrared; Fluoresence

Microwave spectroscopy for compound identification.	W. O. Swan, G. F. Crable and J. C. Wahr
Quantitative analysis by microwave spectroscopy.	G. F. Crable, W. O. Swan J. C. Wahr
Analytical applications of IR spectroscopy with gratings.	G. Kemmner
Analysis of detergents in aqueous solutions using IR spectrometry.	G. Jenkins and D. Ellis
Chemical nature of plastic film surfaces.	M. W. Long, Jr. and J. G. Cobler
Butadiene-styrene copolymer ratio by IR spectrometry.	A. S. Wexler
Quantitative determination of polychloroprene microstructures by IR and NMR spectroscopy.	R. C. Ferguson
Fluorescence of aromatic hydrocarbon-1,3,7,9-*tetramethyluric acid complexes in the solid state.*	B. L. van Duuren and C. E. Bardi
Polarization of steroid fluoresence.	H. S. Strickler and R. C. Grauer

Infrared-Spectra and Miscellaneous

Computor handling of spectra—III:—Programmes for evaluation of spectrophotometer performance.	A. Savitzky and J. M. Roche
Identification of IR spectra by computor techniques.	P. Sadtler and J. Birkenstock
A computor analysis of carbon-hydrogen stretching bands in the IR spectra of hydrocarbons.	A. S. Rosenberg and H. F. Smith
Vibrational and NMR spectra of some methyl derivatives of the guanidinium ion.	J. U. Lowe, A. S. Tompa and G. B. Wilmot
IR study of the asymmetric methylene stretching band of alkanes, alkenes, alcohols, phenylalkanes and chloro-, bromo- and iodo-alkanes.	A. S. Rosenberg and H. F. Smith
New group frequency assignments.	H. Szymanski
An IR study of keto-enol tautomerism as a function of sample preparation.	R. T. Conley and J. A. Corrigan
Low frequency O—H . . . O bond vibrations in hydrogen bonded crystals	V. Ananthanarayanan

Further information can be obtained from R. B. Fricioni, Allegheny Ludlum Steel Corporation, Brackenbridge Works, River Road, Brackenbridge, Pa., U.S.A.

Monday–Thursday 23–26 *March* 1964: **Second International Symposium on Advances in Gas Chromatography:** Sheraton-Lincoln Hotel, Houston, Texas.

The programme is as follows:—

Monday, 23 *March: Morning*

Cross-section ionization.	J. E. Lovelock
Concentration and mass flow sensitive detectors in gas chromatography.	I. Halasz
Specific detection of halogens by flame ionisation.	A. Karmen

Monday, 23 March: Afternoon

How to obtain maximum information from a chromatogram: Identification in particular.	A. I. M. Keulemans
Gas chromatographic characterisation of organic substances in the retention index system.	E. Kovats
The specific retentions of monofunctional organic solutes in monofunctional hexadecyl derivatives.	A. B. Littlewood
Pressure volume changes in a gas chromatographic column.	R. P. W. Scott

Tuesday, 24 March: Morning

Gas chromatographic analysis of urinary oestrogens.	H. H. Wotiz
Gas-liquid chromatography of carbohydrates and related compounds.	C. C. Sweeley
Characterisation and estimation of organic amines of biological interest.	E. C. Horning
Gas Chromatographic analysis of catechol amines.	C. J. W. Brooks
A new type of liquid–liquid and liquid–solid chromatography.	E. Bayer

Tuesday, 24 March: Afternoon

Performance of argon detectors in the field intensified current region	J. Z. Knapp
Measurement and interpretation of the C terms of gas chromatography.	J. C. Giddings
Temperature limitations of stationary phases in gas chromatography.	S. J. Hawkes
A new method of measuring the diffusivity in the gas phase and the obstruction factor.	J. H. Knox
Effect of particle-to-column diameter ratio on band spreading.	J. C. Sternberg

Wednesday, 25 March: Morning

Analysis of flavours by gas chromatography.	A. I. M. Keulemans
Analysis of sulphur compounds with electron capture/flame dual channel gas chromatography.	K. P. Dimick
Thermoramic programmed gas chromatography in the separation of very complex mixtures.	C. Merritt, Jr.
Capillary column gas chromatography: Mass spectral analyses of volatiles from orange oil.	R. Teranishi

Wednesday, 25 March: Afternoon

Preparative columns.	C. Y. Sacodynsky
Simulated distillation by gas chromatography.	L. E. Green
Automatic capillary gas chromatography and sampling of distillation products.	D. W. Grant
Air pollution measurements by gas chromatography and flame ionisation detection.	J. L. Monkman

Thursday, 26 March: Morning

Gas chromatographic study of influence of geometry and chemistry of silica surfaces on their separating and adsorption properties.	A. V. Kiselev
Gas chromatography using solid adsorbents.	L. B. Rogers
Applications of isotopic exchange in gas chromatography.	J. Tadmor
Some properties of graphited black and stationary phases in gas chromatography.	I. Halasz

Further information and registration forms are available from Dr. A. Zlatkis, Chemistry Department, University of Houston, Houston, Texas, U.S.A.

Monday–Thursday 12–15 *October* 1964: **19th Annual International Instrument-Automation and Exhibit of Instrument Society of America:** New York City.

Papers are now invited for the above meeting. Individuals active in all major areas of instrumentation, including measurement, information processing and automatic control, should submit abstracts to H. TYLER MARCY, Vice President-Development, General Products Division, International Business Machines Corporation, White Plains, New York, U.S.A. (deadline: 31 March). The theme of the meeting is **World Frontiers in Instrumentation.**

The **American Society for Testing and Materials** has announced the availability of the 32-volume 1964 *Book of ASTM Standards*. This reflects the entire span of today's knowledge of materials and materials testing. Each volume covers a specific field of interest and includes a detailed index, table of contents and numeric list of standards. Beginning with the 1964 edition, the book will be brought up to date and published annually with the various parts available on the same scheduled date each year. There will no longer be supplements.

PAPERS RECEIVED

Chelating radiometric titrations by ion exchange for determination of traces of metals: JIŘI STARÝ, JAROMÍR RŮŽIČKA and ADOLF ZEMAN. (29 *July* 1963).

Chromatography of *p*′-substituted-*p*-hydroxyazobenzenes on alumina-impregnated papers: R. J. T. GRAHAM and C. W. STONE. (9 *November* 1963).

4,5-Diamino-6-thiopyrimidine as a reagent for the spectrophotometric determination of selenium: FRANK L. CHAN. (2 *December* 1963).

Rapid determination of boron in iron and steel by pyrohydrolysis and constant-current coulometry: TAKAYOSHI YOSHIMORI, TOMOO MIWA and TSUGIO TAKEUCHI. (2 *December* 1963).

Contributions to the basic problems of complexometry—XIV: Determination of zirconium, thorium and titanium in the presence of each other: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (2 *December* 1963).

New trace analysis using radioactive isotope: NOBUO SUZUKI. (2 *December* 1963).

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—III: Titrimetric determination of cerium: G. GOPALA RAO, P. KANTA RAO and S. BHANOJEE RAO. (4 *December* 1963).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—VII: Indium and gallium: J. P. JONES, O. E. HILEMAN, JR., A. TOWNSHEND and LOUIS GORDON. (9 *December* 1963).

Precipitation of indium 8-hydroxyquinaldate from homogeneous solution: J. PAUL JONES, ORVILLE E. HILEMAN, JR., and LOUIS GORDON. (9 *December* 1963).

Use of "dead stop" indication of the end-point in chelometric titrations: F. VYDRA and J. VORLICEK. (10 *December* 1963).

The use of a high frequency Tesla discharge tube for the determination of nitrogen and oxygen in helium: P. ELMOTT and R. E. WILSON. (13 *December* 1963).

Silver^{II} in aqueous perchlorate solutions: GARRY A. RECHNITZ and SIDNEY B. ZAMOCHNICK. (24 *December* 1963).

Absorptiometric study of ammonium aurintricarboxylate as a reagent for palladium^{II}: KAILASH N. MUNSHI and ARUN K. DEY. (24 *December* 1963).

Colorimetric determination of cobalt^{II} by a specific spot reaction: M. H. HASHMI, A. A. AYAZ and ABDUR RASHID. (30 *December* 1963).

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following review published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

An International Quarterly Journal

DISARMAMENT AND ARMS CONTROL

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DISARMAMENT AND ARMS CONTROL has been launched to provide an international forum for the discussion of disarmament, arms control and related topics as a means of reducing the manifest dangers in which mankind now stands. Such work has, in the past, been largely undertaken and published within the haven of the research worker's own country, and makes its greatest impact there. It is hoped that this new medium will encourage the exchange of ideas, insights and experience between workers in different countries. It seeks to establish the understandings through which voluntary limitation and elimination of armaments may be reached.

Contents of the first issue

First Step—Sealed Records Caches?, *John C. Polanyi;* The Role of the Neutrals in the Geneva Negotiations, *M. Samir Ahmed;* Violations of Disarmament Agreements, *Richard J. Barnet;* The International Control of Fissile Material Production, *United Kingdom Atomic Energy Authority;* A Proposal for an African and Near-Eastern Zone Free from Certain Weapons, *David H. Frisch;* Obituary: A. V. Topchiev, *C. F. Powell;* Note: Perjury before International Tribunals; Book Reviews; Current Literature and Research.

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