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REVIEW

## COULOMETRY

H. L. KIES

*Laboratory for Instrumental Analysis,  
Technical University, Delft (The Netherlands)*

(Received June 13th, 1962)

## INTRODUCTION

In coulometry, the result of the analysis is calculated from measurements of the charge transfer during an electrochemical reaction by applying Faraday's laws, supposing the reaction runs to completion with 100% current efficiency.

The name of the unit of charge, the coulomb, is included in a significant way — though in a slightly corrupt form — in the word "coulometry".

The definition given implies that no reaction should take place simultaneously which results in a different final product. There is, however, no objection to the conversion being brought about completely or partially *via* an intermediate; in such cases we speak of "indirect coulometry".

Actual conditions do not always entirely correspond with the ideal situation to which the definition refers. This happens when the results are sensibly affected by the residual current, or when the supporting electrolyte is not perfectly pure. By making a correction for this, or by carrying out a pre-electrolysis, the consequences of such deviations — which become evident when micro-quantities have to be determined — can be largely, or wholly, eliminated.

Larger deviations may occur when the reaction does not run to completion, or when its current efficiency is below 100%. If the results are reproducible, it is possible to achieve the proposed aim by using a factor which is determined empirically. It has gradually become customary to include such cases in coulometry as well.

In general, the reaction at the second electrode (auxiliary electrode) will neutralize the process occurring at the working electrode, either wholly or partly. It is then necessary to put the auxiliary electrode in a separate compartment, which is conductively connected *via* a sintered-glass disc (or an ion-exchange membrane<sup>5,6</sup>) to the solution to be determined.

In practice, we have to be able to establish the moment at which the reaction runs to completion. Sometimes the magnitude of the electrolytic current indicates this; in other cases one may choose from various sensitive indication methods, both electrochemical and spectrophotometric, which are known to us from volumetric analysis. Furthermore, the net quantity of the charge (expressed mathematically by  $\int_0^t i dt$ ) exchanged up to that moment at the working electrode, must be determined by some means.

## HISTORICAL ASPECTS

As far back as 1834, FARADAY<sup>7</sup> stated the laws which apply to an electrochemical conversion. The two laws can be combined in one differential equation:

$$i = \frac{n \cdot F}{M} \frac{dg}{dt}$$

where  $g$  is the weight of the substance participating in the reaction,  $M$  is its molecular weight,  $n$  is the number of equivalents, and  $F$  is the Faraday constant.

The value found for the Faraday constant is 96,490.0 coulombs per g equiv.<sup>7a</sup> with an uncertainty of 0.003%. This possible deviation is therefore of no consequence, in comparison with the accuracy aimed at in analysis.

It was not until 1917 that these laws were applied in an analytical method when GROWER<sup>8</sup>, with only simple equipment, made a device for checking the quality of tinned copper wire. This method was reverted to only much later for determining not only metallic coatings, but also coatings of the oxide, the sulfide, or the halide of the underlying metal. Most of the literature about these applications, particularly the older literature, is not to be found under the heading of coulometry, but under (metal) films, (metal) coatings, corrosion films, tarnish films, cathodic stripping, anodic stripping, and oxide layers.

The term *coulometry* was introduced only in 1938 by SZEBELLÉDY AND SOMOGYI<sup>9</sup>, who are the pioneers of coulometry, in so far as its substitution for classical volumetric methods is concerned. Their work was developed later by SWIFT<sup>10</sup> and others into *amperostatic* (also called galvanostatic) coulometry. We may state with certainty that the great development of coulometry, and particularly of this latter branch, is largely due to more widely spread knowledge of polarization curves.

Another branch of coulometry, *potentiostatic* coulometry, can be traced back to a publication in 1942 by HICKLING<sup>11</sup>, which was elaborated further, especially by LINGANE<sup>12</sup>. Although publications in this field, too, appear regularly — a strikingly large number of them originate from reactor centres — still, I am under the impression that this method is applied less frequently in practice than the amperostatic method. Later, when we discuss potentiostatic and amperostatic coulometry, we shall include methods where the constancy of either the electrode potential or the electrolysis current is only approximate.

Later, in the field of trace analysis, yet another method was introduced, in which the potential of the working electrode is controlled in a different way, *viz.* as a linear function of time<sup>13</sup>: this is referred to as *potential scanning coulometry*.

In the literature<sup>14-16</sup> a distinction is made between direct and indirect coulometry. This classification overlaps the preceding one, and in my opinion is of little value. The term direct coulometry is intended to indicate that, from the beginning to the end of the determination, the electrochemical reaction in which the substance to be determined participates is invariably the same.

Apart from the numerous theoretical discussions, summaries, and applications published in books<sup>17-20</sup> and periodicals<sup>16,21-38</sup>, the growing importance of coulometry is shown by the publication of a good monograph, written by ABRESCH AND CLAASSEN<sup>39</sup>, which is very useful, in particular for those who want to apply coulometry practically.

There are a number of reasons for this growing interest:

- (1) in the first place, coulometry fits in very well with the tendency towards automation of routine analyses;
- (2) in addition, coulometric principles can often be employed in continuous control of gas and liquid streams, which is important in controlling chemical processes;
- (3) exceptionally great accuracy is obtainable, even in micro- and ultramicroanalysis;
- (4) the possibility of remote control is very attractive in the analysis of radioactive material.

Incidentally, coulometry can be used to establish the number of electrons involved in an electrochemical reaction<sup>40-46</sup>. Coulometry is also suitable for determining rates of reactions, when these are not too fast. Some instances of this are quoted in the literature<sup>47-51</sup>.

A very well-known worker in the field of coulometry, TŮTUNDŽIČ<sup>52</sup>, has advocated for many years past the idea of referring the titre of measured solutions to the coulomb, which really amounts to referring it to the atomic weight of silver. If this suggestion, which has met with some approval<sup>53</sup>, but also according to a discussion report<sup>54</sup> with fundamental opposition, were adopted, the problem of preparing numerous titration agents would, at the same time, cease to exist. But this suggestion cannot become of practical importance until the titres of all solutions now used for titrations can be determined coulometrically.

An objection of quite a different kind may be raised against this suggestion, *viz.*, that the titre, expressed in coulombs/litre, is not identical under different circumstances in redox titrations. This objection, of course, holds good equally for the use of the term normality in volumetric titrations. Accordingly, it is advisable to reduce the titre to molarity.

#### MEASUREMENT OF NET CHARGE TRANSFER

Many methods are known for determining the current-time integral. The application of older methods entails performing a number of cumbersome or unpopular operations before the result can be calculated. The newer methods, on the other hand, do call for the use of complicated equipment, but their operation is much simpler. It is, therefore, likely that the older methods are doomed to disappear, because of current analytical trends. It is only for calibration of the newer equipment that they may be used again.

##### A. *Electrolytic coulometers*

A second cell is included in the circuit in series with the electrolytic cell used for the analysis. The products formed in this cell can be measured in four different ways. (1) With *electrogravimetric coulometers* the change in weight of one of the electrodes is a measure of the charge transferred. This method is very suitable for micro-analyses. (2) By measuring the volume of gas formed in the *gas coulometer* the number of coulombs can be calculated, if the pressure and the temperature of the gas are known. The best known example of this method is the oxygen-hydrogen coulometer<sup>12</sup>. Nevertheless, at certain current densities this coulometer may show a deviation due to the simultaneous formation of small amounts of hydrogen peroxide. The nitrogen-hydrogen coulometer, developed much later by PAGE AND LINGANE<sup>55</sup>, does not pre-

sent drawbacks of this kind. In this apparatus a solution of hydrazine sulphate is electrolysed.

(3) In the *titration coulometer*, the contents of one of the electrode compartments are titrated after completion of the electrolysis. I am under the impression that this method is passing into disuse.

(4) A coulometer of recent date is the *coulometric coulometer*<sup>56,57</sup>, which can be regarded as a modern version of the electrogravimetric coulometer. However, instead of determining the increase in weight of one of the electrodes, this coulometer, after completion of the determination, is included in another circuit, by means of which a perfectly constant current is passed through the coulometer in the opposite direction. In this way the electrodes are returned to their original condition. The time required for this, multiplied by the current intensity, gives the number of coulombs consumed for the actual determination. This method is particularly suitable for analyses on a micro-scale. To ensure accurate measurement of the time, the current intensity has to be adapted to the result to be expected.

### B. Calculation for amperostatic (galvanostatic) analyses

The charge can be determined with very great accuracy if the analysis is carried out using a perfectly constant current intensity, even if very small charges are involved (hence its application in coulometric coulometry). The current-time integral then simply becomes the product of the current intensity and the time; these two quantities, therefore, must be determined.

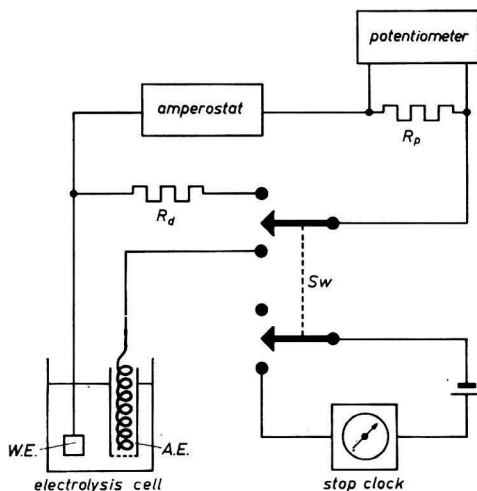


Fig. 1. A circuit widely used for amperostatic coulometry.  $R_d$ , dummy resistor;  $R_p$ , precision resistor; W.E., working electrode; A.E., auxiliary electrode; Sw, switch.

The current intensity is calculated from the voltage drop across a precision resistor incorporated in series with the electrolytic cell. This potential difference can be measured very accurately with a compensator<sup>58</sup>, particularly if the precision resistor has a size, such that the voltage drop across it is about 1 V. The accuracy of the



current intensity thus calculated *via* Ohm's law is always much greater than that attained by using a direct-indicating ammeter.

For measuring the time, a stop-clock which is started and stopped electromagnetically, or an electric clock operated by a constant frequency source can be used<sup>59</sup>. This is done simultaneously when the current is connected and disconnected by means of a single-throw, double-pole switch, or a combination of a simple switch with a double-throw, double-pole relay. If, for one reason or another, it is necessary to interrupt the electrolytic current frequently towards the end-point, a small error may result, especially if the duration of the electrolysis is rather short.

The cause may be a small imperfection in the switch, or in the mechanism for starting and stopping the stop-clock. LINGANE<sup>60</sup> found an error of about 1/50 sec per interruption for his device. The error found in one of our devices was of the same order of magnitude, *viz.* 1/30 sec<sup>61</sup>. This was established by comparison with the measurement of time according to VORSTENBURG AND LÖFFLER<sup>62</sup>, where no errors due to mechanical inertia are possible. In this device a zener diode is also

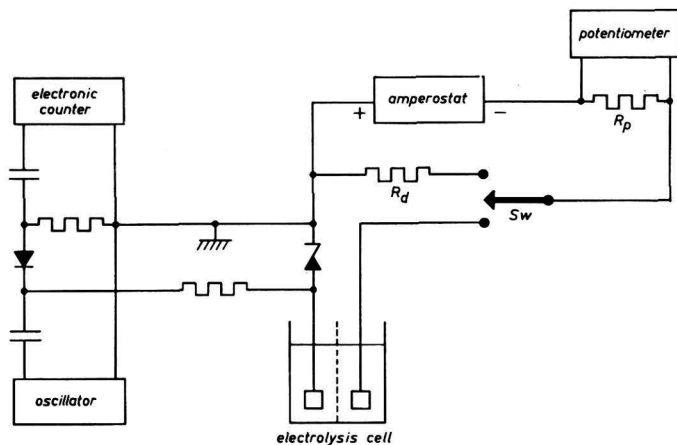


Fig. 2. Circuit for amperostatic coulometry, with an improved device for time measurement according to ref.<sup>62</sup>.

connected in series with the electrolytic cell and the precision resistor. As soon as the electrolytic current, which may vary between 0.25 and 200 mA, is connected across the zener diode a potential difference of about 6 V is set up. This potential difference is set up at the germanium diode OA81, and the latter receives the positive pulses from the oscillator, which are then supplied to the electronic counter.

Another method is due to DEVANATHAN AND FERNANDO<sup>63-65</sup>. In their method, by means of a multivibrator generating device, square (at least in principle) current pulses are forced through the circuit, and the number of pulses counted. This counting, or — what is almost the same — time measurement is not affected by the mechanical inertia of the relay included in the circuit, which has to put the counter in action. In this respect, this method is equivalent to normal amperostatic coulometry combined with time measurement according to VORSTENBURG AND LÖFFLER; the cost of the equipment in the latter case, however, is much greater. On the other hand,

in comparison with the method for determining the current intensity, that of measuring the magnitude of the pulse is much less accurate. Hence, the authors calibrated their device by carrying out an analysis for which they chose a substance which, according to data from the literature, yields good results. The absolute character, typical of coulometry, is lost in this way. The standard deviation, calculated from six analyses, was 1.5<sup>0</sup>/100 and accordingly satisfies normal requirements. It would have been more obvious to use a silver or silver halide coulometer for the calibration.

### C. Electromechanical current-time integrators

Integration is possible in a very simple, and at the same time inexpensive, way by incorporating a resistor in the circuit. The ends of the resistor are connected to one of the coil windings of a low-inertia integrating motor<sup>66-70</sup>. The number of times it revolves within a given voltage range across the resistor is proportional to the current intensity. Mounted on the shaft of the motor is a counter, on which the number of revolutions can be read. This number is proportional to the charge which has moved through the electrolytic cell. The proportionality factor has to be determined for a number of values of current intensity by comparison with an absolute method, because this factor is dependent to some extent on the velocity of rotation.

Apart from the much higher cost, one might, in principle, also use a recording millivolt meter equipped with an integrator, such as is used in gas-liquid chromatography.

A much higher degree of accuracy than with the above methods can be attained by using some other devices, but these are not yet to be found among commercially available apparatus. They are referred to in the literature<sup>71-74</sup>.

### D. Electronic integration

Using exclusively electronic aids it has been possible to carry out the integration of the current-time integral, even when small charges are involved, while the accuracy leaves nothing to be desired. The complicated character of the equipment, however, is likely to bar large-scale application for the present<sup>5,75-76</sup>.

## COULOMETRY WITH CONTROLLED POTENTIAL OF THE WORKING ELECTRODE

### A. Potentiostatic coulometry<sup>17</sup>

It is only by making use of a current-potential diagram, recorded with the same electrode material, that this form of coulometry can be applied in a justifiable way. In direct potentiostatic coulometry the electrode potential is chosen somewhere in the range where the first wave reaches its limiting value (Fig. 3). Beyond this range a second substance would react at the same time. This is inadmissible because of the desired selectivity, whilst at a potential at which the wave is not yet fully developed the duration of the electrolysis becomes unnecessarily long, because the current intensity remains below the maximum value possible for the desired reaction. Once the first component has reacted completely, the second component can be deposited by a change of the potential, and so on.

To save time, it is advantageous in indirect potentiostatic coulometry to choose

the potential in the range of the second wave (Fig. 4). The plutonium analysis of SHULTS<sup>78</sup> is probably the only example of this. In the initial stage,  $\text{PuO}_2^{2+}$  and  $\text{Fe}^{3+}$  are present in the solution; next, reduction to  $\text{Pu}^{3+}$  and a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  takes place. This process is followed by oxidation to  $\text{Pu}^{4+}$  and  $\text{Fe}^{3+}$ . By using this procedure, interference caused by the possible presence of uranium is avoided.

Simpler examples, in which no current reversal is required, can be expected, among

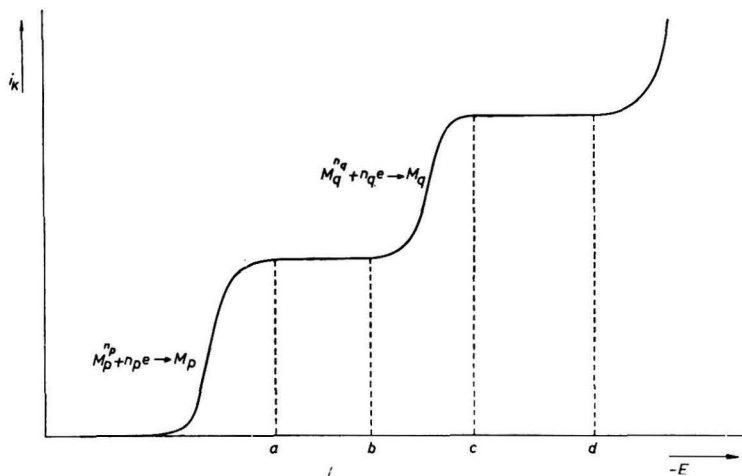


Fig. 3. Potentiostatic coulometry. Metal  $M_p$  is deposited when a potential between  $a$  and  $b$  is applied to the working electrode. After this process has finished, metal  $M_q$  can be deposited by applying a potential between  $c$  and  $d$ .  $E$  is the electrode potential;  $i_K$  is the cathodic current.

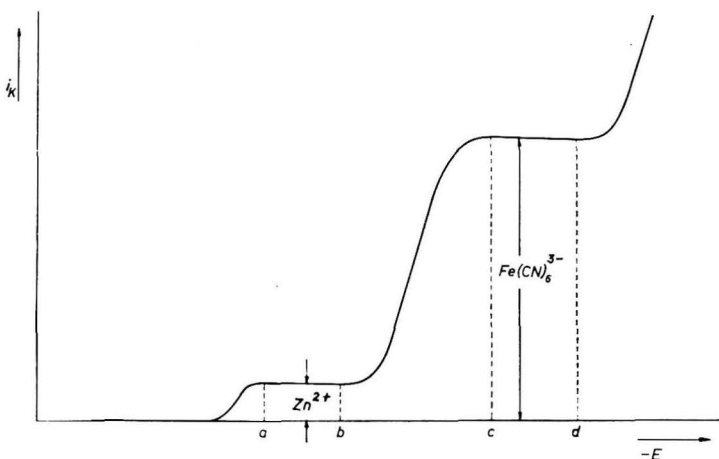
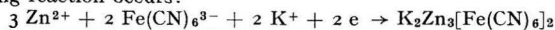


Fig. 4. Potentiostatic coulometry. Determination of  $\text{Zn}^{2+}$ . When a potential is applied between  $a$  and  $b$ , the following reaction occurs:



After electrochemical generation of  $\text{Fe}(\text{CN})_6^{4-}$ , the same precipitate is also formed by chemical reaction in the potential range between  $c$  and  $d$ .

others, in the determination of zinc after addition of cyanoferrate(III) or mercury(II) ethylenediaminetetraacetate to the solution.

In general, a shortening of the reaction time is aimed at by stirring effectively, as a result of which the influence of the background current is reduced considerably<sup>79</sup>, and by making the surface area of the working electrode as large as possible. In micro-analysis the duration, obviously, no longer plays a part.

Because the current intensity in potentiostatic coulometry is much greater as compared with polarography and amperometry, the electrode potential cannot be adjusted in an equally simple way, *i.e.* with the aid of a potentiometer. Hence, a potentiostat is usually used, by means of which the electrode potential is automatically kept constant with fairly great accuracy (1–5 mV). The more recent equipment is fully electronic, and consequently almost without inertia. The potentiostat was introduced in electroanalysis earlier, *viz.* in electrogravimetry, and made rather difficult electrolytic separations possible.

There are sometimes circumstances in which the electrode potential need not satisfy such rigorous requirements; in these cases it may even happen that internal electrolysis is applied<sup>80</sup>.

When the deposition of metals is involved, a platinum electrode can be used in only a few cases, because hydrogen is usually evolved at the same time. This obviously can not be tolerated in coulometry; hence, as in polarography, mercury was introduced as the cathode material<sup>12</sup>. An additional advantage is that the polarograph can be used for introductory investigation of the optimum conditions.

If there are no complications in the reaction at the working electrode, the current intensity can be calculated at any instant during the analysis, provided the volume of the surface layer round the electrode is negligible in proportion to the whole volume. The derivation is as follows: at a potential at which there is a question of a limiting current, the number of particles reacting at the electrode per unit of time is proportional to the concentration  $*C$  in the bulk of the solution, *i.e.*  $dN/dt = k *C$ ;  $k$  depends on the size of the electrode and the stirring speed. This involves a lowering of the concentration of the solution, *i.e.*,

$$V \frac{d*C}{dt} = -k*C$$

where  $V$  stands for the volume.

This differential equation can easily be integrated:

$$\ln *C = -kt/V + a$$

(where  $a$  = integration constant). For  $t = 0$  we have  $*C = *C_0$  (initial concentration), so that

$$\ln *C/*C_0 = -kt/V$$

Since

$$i = nF \frac{dN}{dt} = nFk*C$$

we have

$$i/i_0 = e^{-kt/V}$$

( $i_0$  = initial current intensity). The current intensity thus decreases according to an e-function. With the aid of the last expression the magnitude of the charge transfer can also be calculated:



$$\int_0^{\infty} i dt = i_0 V/k$$

If the logarithm of the current intensity is plotted *vs.* time, the value of the integral can be found by using this graph. In fact, the slope of this straight line furnishes the factor  $k/V$ , while extrapolation to  $t = 0$  gives the initial current intensity  $i_0$  with greater accuracy than is possible by direct measurement. Because the current intensity  $i$  is proportional to the concentration  $*C$  in the bulk of the solution, we may assume that when  $i$  has decreased to  $1^0/_{00}$  of the initial value the reaction is complete, but for  $1^0/_{00}$ . If the determination is stopped at this moment, therefore, a correction can be made.

Another graphical method, due to HANAMURA<sup>73</sup>, plots the function  $\int_0^t i dt$  *vs.* the current intensity  $i$ . Extrapolation to  $i = 0$  gives the required value. For this, a current-time integrator, which can be read directly, must be included in the circuit. An almost identical method of calculation is that of MEITES<sup>81</sup>.

It is obvious that a graphical method, whose application is not always permissible, must not be expected to produce extreme accuracy. It is an advantage that the electrolysis can be terminated sooner, at least if no second substance has to be dealt with subsequently. In general, other (previously discussed) methods are employed.

The concentration range over which potentiostatic coulometry can be applied varies for each individual case. The maximum upper limit is about 2 mequiv., ( $\text{Br}^-$ <sup>82</sup>) and the minimum lower limit is  $5 \cdot 10^{-5}$  mequiv., ( $\text{Zn}^{2+}$ <sup>83</sup>). The determination of micro-quantities makes it essential to consider the residual current, which occurs in any electrolysis to some degree. Because the magnitude of the residual current is affected by many factors, it is by no means easy to make a correction in the right way. This aspect has been dealt with extensively in the literature<sup>84,84a</sup>.

In the field of organic analysis this method has so far seldom been applied. Examples are the nitro compounds<sup>79,85,86</sup>, the halogen compounds<sup>86</sup>, ascorbic acid<sup>87</sup> and anthraquinone<sup>88</sup>.

### B. Potential scanning coulometry

This method is employed exclusively in micro-analysis. The object of the first phase, the so-called pre-electrolysis or plating cycle, is to deposit the substance to be determined on an electrode, thus concentrating it. For practical reasons it is not customary to wait until this process has run to completion. Even an efficiency of 80% requires a good deal of time at room temperature<sup>13</sup>. If constant efficiency is to be ensured identical times for deposition must be used for each set of determinations. During the second phase of analysis the electrode is freed of its deposit by changing the potential continuously: in view of the low current intensity, a polarograph can be used for this. This process proceeds quantitatively. The polarograph records a curve with a peak near the half-wave potential. A curve is also recorded using a blank; this curve, which is ascribed mainly to the condenser current<sup>13</sup>, resembles a truncated parabola. The area between the two curves is a measure of the charge required to free the electrode of the deposit. It is found to be proportional to the quantity of substance originally present in the solution<sup>13,89,90</sup>. Recently, an accurately centred, rotating, mercury-plated platinum electrode was introduced for the same purpose<sup>91,92</sup>.

All methods mentioned above require calibration curves, obtained by plotting coulombs *vs.* concentrations. Consequently, the absolute character, which is typical of coulometry, has been lost.

This has become the case to an even greater degree, owing to the introduction of a simplified process, in which it is no longer the area which is measured, but the peak height of the curve, measured with reference to the blank determination<sup>93-95</sup>. Properly speaking, it is illogical to use the name coulometry for this method. (In the recently published nomenclature proposal no provision was made for this<sup>96</sup>.) When the analysis of traces is involved, this method yields excellent results. The lower limit of analysis is about  $10^{-8}$  *M*, depending on the volume, while the accuracy is quite reasonable. The adoption of the hanging mercury drop has greatly improved the reproducibility<sup>97-105</sup>.

#### AMPEROSTATIC COULOMETRY

If the number of publications about a particular technique is a measure of its actual use, amperostatic is undoubtedly superior to potentiostatic coulometry. This is probably due to several causes, *e.g.* a given degree of accuracy is attained more readily with amperostatic than with potentiostatic coulometry, especially when requirements are very exacting. A further important aspect is that numerous classical titrations can be automatized without the use of mechanical aids.

In the many cases where extreme accuracy is not required, a current intensity that is kept rigorously constant, and consequently the use of an amperostat, can be dispensed with. The charge can then be measured quite conveniently with an integrating motor<sup>106</sup>, especially because we are then in the favourable position of having a current intensity which varies very little. As a result, the ratio between the number of revolutions and the charge remains constant throughout the analysis. It was observed above that this is only approximately so in potentiostatic coulometry. A number of these simplified devices, which are correspondingly less expensive, have recently become commercially available.

In these applications, the determination of the thickness of surface layers occupies a separate place and will be discussed later.

In analysing solutions, the end-point was originally shown by indicators. Later, electrochemical indicating methods were preferred. This involved difficulties when fairly large amounts, *e.g.* of the order of magnitude of 1 mequiv. were to be analysed. As a matter of fact, a large generating current (*i.e.* the electrolytic current causing the desired reaction) affects the indicating current. Reduction of the intensity of the generating current is not practical, because the reaction takes longer for completion. An improvement is seen when one of the two electrodes incorporated in the indicating circuit surrounds the other<sup>34,107,108</sup>. A more radical method was the formation of a suitable reagent electrochemically outside the solution. This is called *external generation*, in contrast with the older method with internal generation, which is generally preferred.

Another reason for applying external generation may arise when conditions which hold good for obtaining the intermediate with 100% efficiency cause an unacceptably low rate of reaction between the substance to be determined and the intermediate. An example is the titration of dyestuffs with titanium(III).

### A. Determination of the thickness of surface layers

Metals such as silver and copper, when exposed to the atmosphere, tend to lose their brightness owing to the formation of a tarnish film. Sometimes such a film is deliberately produced to prevent attack of the underlying metal. For the same purpose, some metals are provided with a thin film of another metal; the tinning of iron is an instance of this.

Checking the quality entails determining the thickness of the surface layer. The older procedure is based on selective chemical attack, usually of the film, but sometimes also of the underlayer. In many cases the application of galvanostatic coulometry now offers considerable simplification. Devices specially designed for this purpose have already become commercially available; the potentiostatic method has not found acceptance.

The material must be placed in the electrolytic cell in such a way that only the surface layer can be attacked electrochemically. This is most simply done by coating the underlayer with a chemically resistant varnish. For sheet material special cells have also been designed. One of these is a Plexi-glass cylinder, against the underside of which the sample, cut to the proper size, is forced by means of a screw-top. Uniform current density is desirable.

The choice of the supporting electrolyte must be determined empirically for each individual case. Indication takes place exclusively potentiometrically. For this purpose a third electrode is placed in the cell as a comparison electrode. At the end of the analysis the working electrode passes through a number of incompletely investigated states, when the material is not fully coated any longer; after this, a second process commences. This transition is accompanied by a fairly abrupt change of the electrode potential. The thickness  $d$  can be calculated from the equation:

$$d = \frac{itM}{nFA\rho}$$

in which  $d$  is the thickness in cm,  $i$  is the applied current in ampères,  $n$  is the electrochemical equivalent,  $t$  is the time in sec,  $A$  is the surface of exposed specimen in sq. cm,  $F$  is the Faraday constant,  $M$  is the molecular weight, and  $\rho$  is the density of the surface layer. An accuracy of within 2% is claimed.

During the tinning of iron and copper a portion of the tin forms an alloy with the underlying metal (FeSn<sub>2</sub> and Cu<sub>3</sub>Sn, respectively). The presence of the iron-tin alloy is revealed in the potentiogram by a second jump; with copper only one jump is present when the free tin has gone into solution; the disappearance of the alloy can be observed by a change of colour. It is important to analyse each layer individually, because the iron-tin alloy is of little value for protection from corrosion as such, but it is valuable for adhesion.

For the first time in the literature, those combinations of metals used in surface coatings and already analyzed by this method are summarized (surface layers come first).

*Metallic coatings:* Ag/Fe<sup>109</sup>; B/Pt<sup>110</sup>; Cd/Fe<sup>109,111</sup>; Cr/Cu<sup>109,111,112</sup>; Cr/Fe<sup>109,112</sup>; Cr/Ni<sup>111,113</sup>; Cu/Fe<sup>109,111</sup>; Ni/Cu<sup>111</sup>; Ni/Fe<sup>111</sup>; Pb/Cu<sup>109</sup>; Pb/Fe<sup>109</sup>; Sn/Cu<sup>8,109</sup>; Sn/Fe<sup>109,114-123</sup>; Zn/Cu<sup>109</sup>; Zn/Fe<sup>109,111,124-126</sup>.

*Other films:* AgI/Ag<sup>127-129</sup>; Ag<sub>2</sub>S/Ag<sup>130,131</sup>; Cu<sub>2</sub>O/Cu<sup>132-138</sup>; Cu<sub>2</sub>S/Cu<sup>131,134,138</sup>; iron oxides/Fe<sup>133,139</sup>; SnO/Sn<sup>121,123,140-143</sup>.

Most of the literature is to be found in technical periodicals.

The method just described was first applied by ZBINDEN<sup>144,145</sup> for determining traces of cations. The procedure has been described more fully by ELEMA<sup>146</sup>. The solution in which the cations are present is first electrolysed, and the cations being investigated are deposited on the cathode. Next, a constant current is passed in the opposite direction, which frees the electrode of its deposit. The results calculated from the product of current and time indicate that this method produces quantitative results for amounts of 6–2500  $\mu\text{g}$ .

For much smaller quantities this method has been replaced by potential scanning coulometry; application of the potentiostatic method for bringing the originally deposited metal into solution again has only been mentioned once<sup>94</sup>.

Presumably the recently introduced acetylene black electrode<sup>147</sup> will have potentialities in organic analysis. In the first stage of the process the substance is absorbed from its solution (usually in an organic solvent) into the carbon black. Next, the carbon paste is impregnated with a concentrated aqueous salt solution (*e.g.* zinc chloride with ammonium chloride). A constant current is then forced through this solution *via* the carbon electrode and a second electrode. The end-point of the electrochemical process is established potentiometrically.

### B. External generation

Because of its simplicity, which makes an explanation hardly necessary, this method is discussed first, although internal generation is an older method.

The problem of providing the generator circuit externally can be solved simply. In the oldest device<sup>58,148–151</sup> a siphon made from a glass capillary is used. In the middle there is a small widening, in which a T-joint is made. (The whole device has the form of a hollow, two-pronged fork.) The glass tube is connected to a liquid reservoir. Platinum electrodes are sealed on either side of the T-joint and are connected to the circuit, giving a constant current intensity. The liquid flowing from the reservoir leaves the siphon on either side. When a solution of sodium sulphate is supplied, sulphuric acid is formed at the anode, and sodium hydroxide at the cathode. According as to whether an acid or a base is to be titrated, the titration vessel is mounted underneath the cathodic or the anodic limb. If a bromination is to be performed, potassium bromide is used as the electrolyte and the anodic limb is used. One half of the liquid is thus continuously discharged and lost. If current efficiency of 100% is to be ensured, the concentration of the electrolyte supplied has to be sufficiently high; in addition, as large an electrode surface area as possible is desirable.

Later on, a single-armed generator cell was also designed<sup>152–153</sup>, in which the working electrode is again present in the stream of liquid, but the second electrode is located in the reservoir behind a glass diaphragm.

A single-armed cell, which ensures even more effectively that the products of the electrolysis formed at the auxiliary electrode cannot diffuse towards the working electrode, was designed by QUADT as a generator cell<sup>154,155</sup>. The liquid reservoir is connected to a porous earthenware tube, the lower end of which is connected to a capillary. The roll of platinum gauze present inside the porous tube acts as the working electrode. The current is fed to this electrode *via* a platinum seal in the capillary. Surrounding the porous tube is a cylindrical space, at whose outer surface the auxiliary electrode is fixed. This space is filled not only with the same electrolyte that



moves along the working electrode, but also with an ion exchanger, which removes the product of the electrolysis from the auxiliary electrode. This provides a better guarantee that no diffusion towards the working electrode shall take place. In all the devices it is possible to avoid an error due to any holdup in the capillary between the working electrode and the solution by simply fitting a flush-out tube<sup>148</sup>.

Determinations performed with external generation hardly differ from normal volumetric methods in essentials; the only difference is that the titre is no longer referred to the unit of volume, but to the unit of time. Moreover, in redox titrations the value of the redox potential may sometimes become rather unfavourable, owing to the presence of a large excess of the other, non-active component of the redox couple, which is supplied simultaneously with the reagent.

### C. Internal generation<sup>37,38</sup>

When the working electrode is located in the titration vessel and the current intensity is kept constant, it is usually impossible to cause the substance originally present to react directly from the beginning of the reaction to the end with 100% current efficiency.

This again can be explained by means of current voltage diagrams, but in contrast

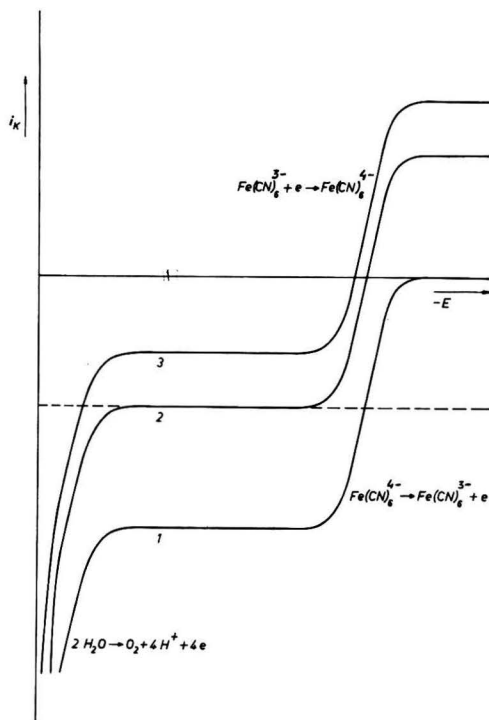


Fig. 5. Amperostatic coulometry of  $\text{Fe}(\text{CN})_6^{4-}$  at a platinum working anode. ---, indicates the applied current (also in the following figures). Voltammograms of: (1), the initial state; (2), an intermediate state at the limiting case of 100% efficiency; (3), a state some time afterwards. The efficiency has fallen considerably below 100%.

with potentiostatic coulometry, an accurate knowledge of the values on the potential axis is generally not necessary.

Let us take, as an example, the determination of potassium cyanoferrate(II), a compound which can be converted at the anode into potassium cyanoferrate(III). (See Fig. 5.) Before the determination starts there is only an anodic wave. If the current intensity applied is smaller than the value of the anodic limiting current, all the charge supplied will be used for the conversion to cyanoferrate(III). This results in the anodic wave decreasing proportionally with time and in a cathodic wave being produced, which increases proportionally with time. At a given moment the anodic limiting current will equal the current passed. This is the case when the part of the substance not yet converted is equal to the ratio between the actual current intensity and the initial value of the anodic limiting current. As soon as this moment has passed, continued electrolysis causes a decrease in the anodic limiting current, but this decrease is no longer proportional to the duration of the electrolysis. This is due to the fact that the difference in magnitude between the limiting current and the current passed causes decomposition of the supporting electrolyte. (This situation may also present itself from the beginning, depending on the applied current intensity.) It is indeed conceivable that the oxygen evolved at the anode as a result might enter into a chemical reaction with the cyanoferrate(II), but actually the velocity of this reaction is insufficient for it. The product of  $i$  and  $t$  is, thus, no longer a measure of the quantity of the cyanoferrate(II) originally present.

A slightly less unfavourable situation occurs with the oxidation of iodide to iodine. When the generating current becomes larger than the limiting current of the first

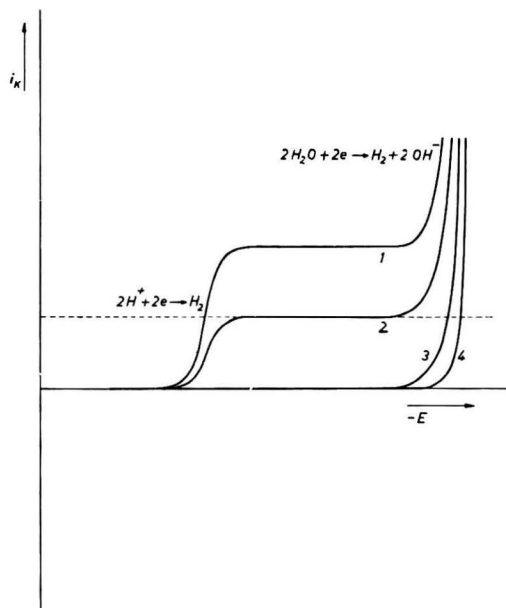
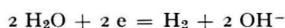


Fig. 6. Amperostatic coulometry of a strong acid at a platinum working cathode. Voltammograms of: (1), the initial state; (2), limiting the case of 100% efficiency for the primary reaction; (3), conditions when the reaction is complete; (4), conditions after equivalence has been reached. (1, 2, 3 and 4 also apply in the following figures.)

iodide wave, the second reaction taking place is the oxidation to iodate<sup>156</sup>. The iodate reacts in the acid medium with the remaining iodide to form iodine. As the heights of the first and second waves are in a fixed ratio to each other, the supporting electrolyte will be oxidized in a further stage, so that again the aim is not achieved immediately.

However, there are a few exceptional cases where the aim is achieved without any additional precautions. These will be explained more fully, because this leads to the solution of the above-mentioned problem.

For the first example, consider the determination of a strong acid<sup>9,157,158</sup>. At first,  $\text{H}_3\text{O}^+$  ions discharge, (see Fig. 6), with evolution of hydrogen, until a second, additional electrochemical reaction begins, according to the equation,



The hydroxyl ions thus formed then enter into a chemical reaction with the hydrogen ions still present in the solution. Ultimately, the result of the two reactions is identical, so that in spite of the secondary electrochemical reaction, the aim is still achieved. In this case we speak of a primary coulometric titration<sup>160</sup>.

The other exceptions occur when the electrode material itself participates in an anodic process. These cases are grouped together under the name of metallometry<sup>31,161</sup>. The first example is the determination of chloride using a silver anode<sup>60</sup> (see Fig. 7).

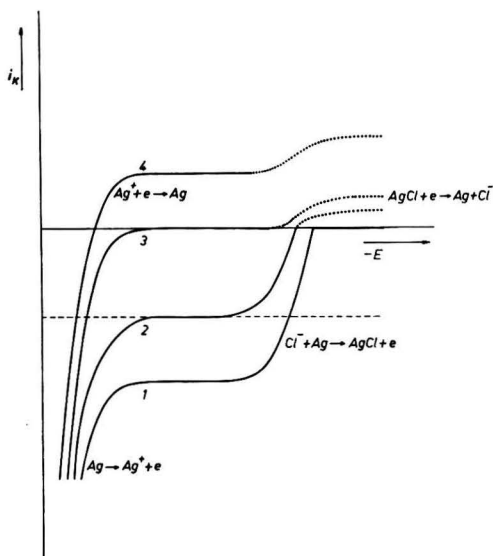
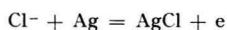


Fig. 7. Amperostatic coulometry of chloride ion at a silver working anode. . . . , probable course of the curve in the presence of a suspension of  $\text{AgCl}$ .

The equation for the primary reaction is:



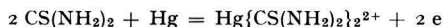
As soon as the limiting current, which refers to the supply of  $\text{Cl}^-$  ions to the anode,

has become smaller than the current passed, a second reaction takes place at the anode, *viz.*



after which the silver ions form silver chloride with the chloride ions left in the solution. Some related reactions are also known<sup>162,163</sup>.

A second example is the determination of thiourea<sup>164</sup> and aliphatic N-substituted derivatives<sup>165</sup> using a mercury anode. Here the primary reaction is:



Towards the end of the determination the following additional reaction takes place (see also Fig. 8):

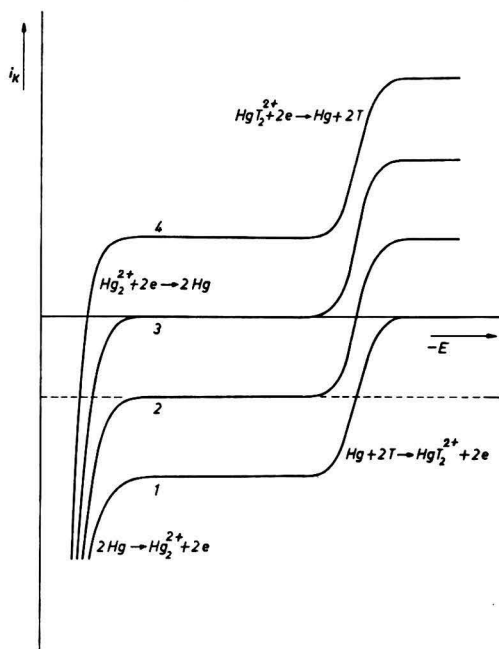
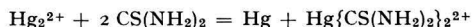


Fig. 8. Amperostatic coulometry of thiourea (T) at a mercury working anode.

The mercury(I) ions react, with dismutation, with the remaining thiourea according to the following equation:



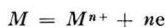
The complete conversion of thiourea into its mercury(II) complex thus requires *one* electron per molecule of thiourea.

The dismutation is not the essential thing in the determination of complex-forming substances. It is inherent in the use of a mercury anode, known exceptions being the determination of cyanide in alkaline medium<sup>166</sup> and determination of dithiocarbamic acid in the presence of acetone<sup>167</sup>. (In the former case mercury(II)



oxide may be formed as an intermediate, and in the latter case the mercury(II)-acetone complex.) If, for instance, the formation of a complex silver compound forms the basis of a determination, dismutation does not occur.

A galvanostatic determination of the content of an amalgam also occurs in part *via* an indirect method<sup>168</sup>. As long as the generating current passing through the circuit is smaller than that corresponding to the height of the (anodic) diffusion wave of the metal  $M$  dissolved in mercury, the metal goes directly into solution according to the equation:



When, owing to depletion of the amalgam, the height of the anodic wave becomes

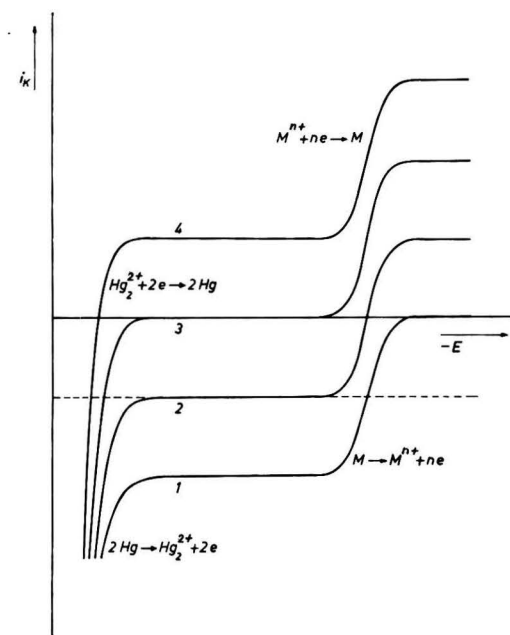
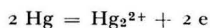


Fig. 9. Amperostatic coulometry of an amalgam.

lower than corresponds to the generating current (Fig. 9), a second reaction takes place in addition to the electrochemical reaction described above, *viz.*:



This is followed by the purely chemical reaction (which, moreover, is heterogeneous):



The result of the two last reactions is again the same as that of the direct reaction. (In the presence of chloride, mercury(I) chloride is the intermediate.)

In all the exceptional cases discussed, the desired reaction is brought about with interchange of the theoretically calculated quantity of charge, but this partly takes place by means of a second electrochemical reaction, followed by a consecutive, purely chemical reaction. This principle can also be applied to the general cases. In fact, if it were possible, by means of a secondary electrode reaction, to generate

a substance which is able to react rapidly and completely with the substance to be determined, the charge passed would fully benefit the contemplated reaction. In the example of cyanoferrate(II) discussed above, the object is achieved completely by the addition of potassium bromide. Before the supporting electrolyte can be attacked, bromine is formed at the anode, which is able to react with cyanoferrate(II) with back-formation of bromide. (Fig. 10).

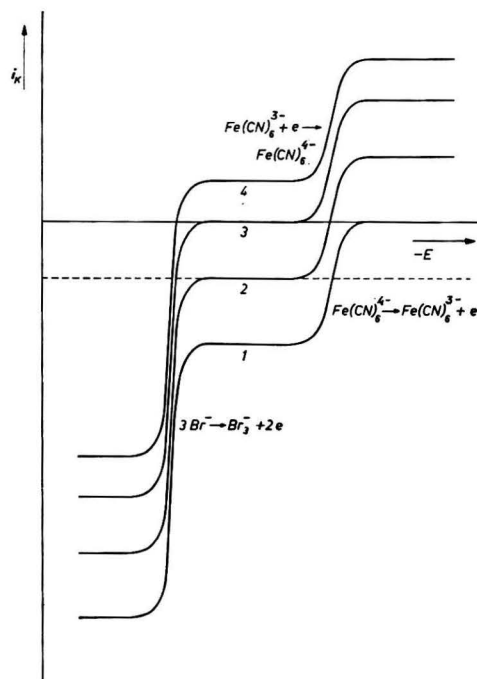


Fig. 10. Amperostatic coulometry of  $\text{Fe}(\text{CN})_6^{4-}$  after addition of bromide. The efficiency remains 100% even after having reached state (2).

Preferably, an auxiliary substance is chosen from the series of reversible redox couples, because a knowledge of their standard potentials simplifies the choice, and also because experience has taught that the reaction rate between components of rapid redox system is also high. This method is frequently referred to as *secondary coulometric titration*<sup>160</sup>.

In the example under discussion, therefore, two redox systems occur, *viz.* cyanoferrate(III)–cyanoferrate(II) and tribromide–bromide. The standard potentials of these systems are 0.36 V and 1.05 V respectively, *vs.* N.H.E.

The rule holding for determining a substance belonging to a *reversible* redox system is that the standard potential of the auxiliary system has to lie between the potential of the system to which the reduction or oxidation agent to be determined belongs and the potential at which the supporting electrolyte itself is decomposed, owing to oxidation or reduction. The auxiliary system should be regarded as a redox buffer, *i.e.* a system which greatly restricts the possibility of variation of the electrode potential.

TABLE I  
AUXILIARY SYSTEMS

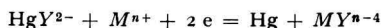
Redox system	Standard redox potential	Literature references
Ag <sup>2+</sup> –Ag <sup>+</sup>	2.0	169
Ce <sup>4+</sup> –Ce <sup>3+</sup>	1.6	156, 170
Mn <sup>3+</sup> –Mn <sup>2+</sup>	1.5	171–176
Cl <sub>2</sub> –Cl <sup>–</sup>	1.36	177, 178
Br <sub>3</sub> <sup>–</sup> –Br <sup>–</sup>	1.05	179, 180
VO <sub>2</sub> <sup>+</sup> –VO <sup>2+</sup>	1.00	181
Fe <sup>3+</sup> –Fe <sup>2+</sup>	0.77	182, 183
BrO <sup>–</sup> –Br <sup>–</sup>	0.76	184
CuBr <sub>4</sub> <sup>–</sup> –CuBr <sub>4</sub> <sup>2–</sup>	0.72	185
I <sub>3</sub> <sup>–</sup> –I <sup>–</sup>	0.54	186
CuCl <sub>4</sub> <sup>–</sup> –CuCl <sub>4</sub> <sup>2–</sup>	0.52	187
Fe(CN) <sub>6</sub> <sup>3–</sup> –Fe(CN) <sub>6</sub> <sup>4–</sup>	0.36	188
UO <sub>2</sub> <sup>2+</sup> –U <sup>4+</sup>	0.33	189, 190
SnBr <sub>6</sub> <sup>2–</sup> –SnBr <sub>4</sub> <sup>2–</sup>	0.27	191–194
FeY <sup>–</sup> –FeY <sup>2–</sup>	0.12	195
TiO <sub>2</sub> <sup>+</sup> –Ti <sup>3+</sup>	0.1	196
HSO <sub>3</sub> <sup>–</sup> –S <sub>2</sub> O <sub>4</sub> <sup>2–</sup>	–0.01	197
Cr <sup>3+</sup> –Cr <sup>2+</sup>	–0.4	198

A great many such auxiliary systems are known; they are included in Table I, which refers mainly to recent literature. In principle, one of the components of an auxiliary system may be used as the titration agent; sometimes, however, difficulties arise, *e.g.* owing to volatilization (Br<sub>2</sub>), oxidation (Ti<sup>3+</sup>), or adsorption (highly dilute titrants).

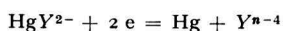
It is very interesting that water determination according to Karl Fischer<sup>199,200</sup> can also be accomplished by the coulometric method. In this case, the reagent has to be modified slightly: the iodine is replaced by iodide<sup>201</sup>.

Besides the above-mentioned auxiliary substances, REILLEY has introduced a very special one, *viz.* mercury(II)–ethylenediaminetetraacetate (abbreviated to H<sub>2</sub>HgY)<sup>202</sup>. The use of this substance (or possibly another complex, such as H<sub>2</sub>CdY<sup>203</sup>) has made it possible to perform complexometry, also by coulometric methods. The slightly different behaviour of this auxiliary substance makes a separate discussion desirable<sup>204</sup>. This behaviour is further determined by the stability of the complex between Y<sup>4–</sup> and the cation M<sup>n+</sup> to be determined with regard to the complex HgY<sup>2–</sup>.

1. HgY<sup>2–</sup> is more stable than MY<sup>n–4</sup>. At first, the following reaction takes place at the cathode (see also Fig. 11):



Later on, when the limiting current relating to this reaction has become smaller than the current passed, a part of the current is consumed for the reaction:



This is followed by the chemical reaction between M<sup>n+</sup> and Y<sup>4–</sup>, so that at the equivalence point all the cations M<sup>n+</sup> have been bound to form MY<sup>n–4</sup>. For this, two electrons per ion of M<sup>n+</sup> have been consumed. Beyond the equivalence point the decomposition of the auxiliary substance continues.

2. HgY<sup>2–</sup> is less stable than MY<sup>n–4</sup>. In view of the values of the stability constants

for the various cations, this case presents itself very rarely. First of all, addition of the auxiliary substance results in the chemical reaction represented below, (see also Fig. 12).

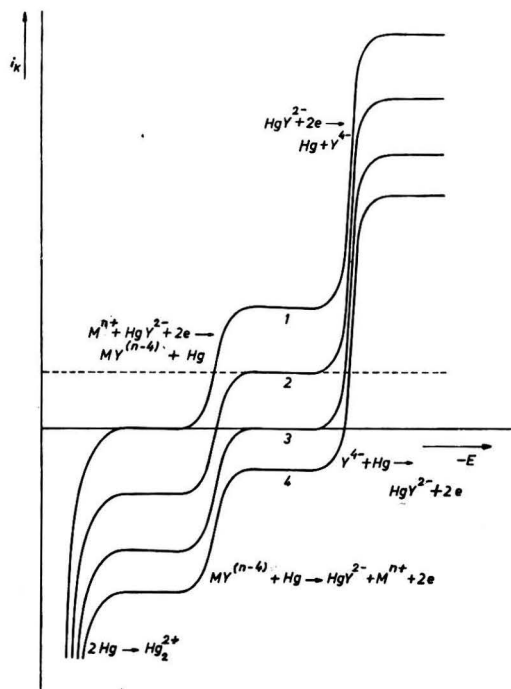
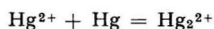


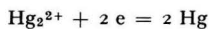
Fig. 11. Amperostatic coulometry of  $M^{n+}$  at a mercury working cathode after addition of  $\text{HgY}^{2-}$ .  $\text{MY}^{n-4}$  is less stable than  $\text{HgY}^{2-}$ .

When a mercury cathode is used, the mercury(II) is subsequently reduced to mercury(I):

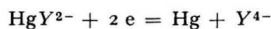


These two reactions accordingly do not yet call for any interchange of electrons.

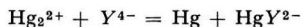
As the current is switched on, the mercury(I) ions discharge up to the equivalence point:



Also, the following reactions occur in the last stage:



and



Again, two electrons per ion of  $M^{n+}$  are required. It is questionable, however, whether the latter reaction proceeds sufficiently rapidly — a condition for a successful determination. There are some indications that the reaction rate between mercury(I) and ethylenediaminetetraacetate is less favourable than it is in the case of the analo-

gous reaction of mercury(I) with thiourea, discussed previously. Beyond the equivalence point, decomposition of the complex  $\text{HgY}^{4-}$  takes place.

Substances behaving similarly are the mercury compounds with thioethyleneglycol<sup>205</sup> and with tetraethylenepentamine<sup>206</sup>.

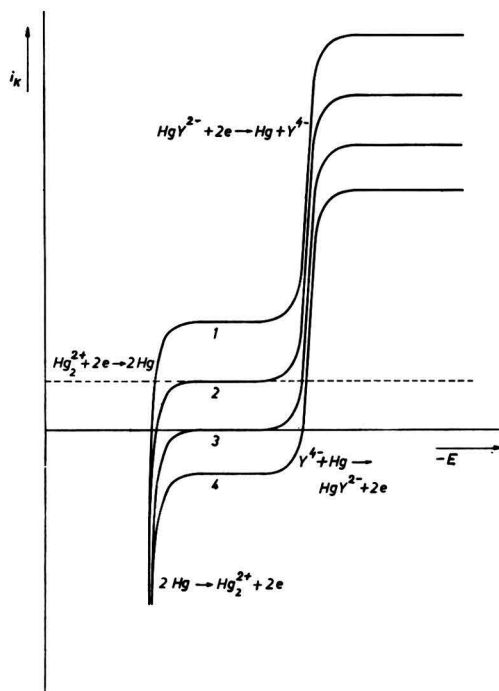


Fig. 12. Amperostatic coulometry of  $M^{n+}$  after addition of  $\text{HgY}^{2-}$ .  $\text{MY}^{n-4}$  is more stable than  $\text{HgY}^{2-}$ .  $\text{Hg}_2^{2+}$ , set free by chemical reaction in an amount equivalent to the initial concentration of  $M^{n+}$ , gives  $\text{Hg}_2^{2+}$  by interaction with the mercury electrode.

Another known auxiliary substance is potassium dicyanoargentate<sup>207</sup>, from which cyanide ions are liberated at a platinum cathode. By means of this system  $\text{Ni}^{2+}$ ,  $\text{Au}^{3+}$ , and, of course,  $\text{Ag}^+$  can be determined.

If the substance to be determined belongs to an *irreversible* redox couple, the above-mentioned rule (p. 274) also applies, provided we bear in mind that the standard potentials refer to equilibria. Because of a large activation polarization, the wave referring to the substance to be determined may have shifted considerably. The supporting electrolyte will sometimes enter into reaction simultaneously with, or even more readily than, the substance to be determined<sup>37</sup>. Examples are the oxidation of thiosulphate<sup>208</sup> and hydrazine<sup>9,209</sup>. In such cases, it is exclusively the auxiliary substance which reacts at the electrode. If the subsequent chemical reaction occurs rapidly, this method produces quantitative results.

The auxiliary substances used in the above examples (thiosulphate and hydrazine) are iodide and bromide, respectively. This choice is not surprising, because it is known from classical volumetric reactions that iodine and bromine, respectively,

(or bromate in an acidified solution of bromide) react very readily with the substances in question.

Many publications have appeared about the chlorination<sup>210</sup>, and particularly about the bromination<sup>10,210-214</sup>, of organic substances. Here, for another, very obvious reason, the auxiliary substance participates in the process from the beginning.

In volumetric work, it is sometimes more favourable to add an excess of the reagent first and then back-titrate the excess with another reagent. The same procedure may sometimes be advantageous in coulometry. For this purpose, a combination of two auxiliary substances is used; only a reversal of the direction of the current is then necessary. Thus, the combination  $\text{KBr}-\text{CuSO}_4$  is very satisfactory for the bromination of organic compounds<sup>215-217</sup>. Another known combination is  $\text{Ce}_2(\text{SO}_4)_3-\text{Fe}_2(\text{SO}_4)_3$ <sup>170,218</sup>, used in the titration of oxalic acid and also  $\text{Fe}_2(\text{SO}_4)_3-\text{MnSO}_4$ <sup>174</sup>.

The auxiliary substance, mercury complexonate, is, in itself, a complex. However, the possibility of quantitative removal of complexon has not yet been investigated.

The determination of small quantities may be hampered by impurities in the supporting electrolyte or in the auxiliary substance. In most cases it is possible to avoid errors by performing several determinations in succession in the same solution, ignoring the result of the first (pre-titration<sup>105,219,220</sup>). Attention should then be given to the correct indication method<sup>221,222</sup>.

By adopting the expression introduced by MYERS AND SWIFT<sup>223</sup>, it has become customary for all those galvanostatic determinations in which an auxiliary substance is required to be called coulometric titrations. In the case of external generation this is very obvious because of the great similarity, which has already been pointed out. The place of the stopcock on the burette is then taken by the switch, with the difference from the burette stopcock that the rate of supply can also be regulated. Another resemblance is found when substances which have slow electrochemical reactions are determined, because the auxiliary substance is then used in the process from the beginning. In the determination of substances which can be classed among the rapid redox systems the name is not quite correct, because during the electrolysis these substances themselves react directly at the working electrode. A further disadvantage of this nomenclature is that it creates the impression that coulometric titrations are comparable with the older electrochemical titration methods, conductometry, potentiometry, and amperometry. The latter, however, are merely indication methods, whilst coulometry deals with a very special kind of reagent supply (or withdrawal), if we consider the reagent to be a stream of electrons<sup>206,224</sup>. In this sense, coulometry can be compared with acidimetry, iodometry, cerimetry, and complexometry, to mention only a few instances. However, the term *coulometric titrations* has become too generally accepted to attempt to abolish this nomenclature because of the objections raised against it.

#### D. Water determination with the Keidel cell<sup>225</sup>

This electrolytic cell occupies an exceptional position in coulometry, because both electrodes are working electrodes. The moist gas flows through a tube, inside which there is a core of glass or teflon, provided with two separate helical grooves. After the platinum electrodes have been fitted in it, the core is coated with a thin film of a highly hygroscopic mixture consisting of phosphorus pentoxide and meta-phosphoric acid. Water, which results from the combustion of organic compounds in elementary

analysis<sup>226</sup>, is temporarily absorbed by the hygroscopic mixture. A constant current is then passed until the tension of the cell has risen to the original value (about 75 V). The reaction mechanism has not yet been investigated, but recently a hypothesis was put forward<sup>267</sup>. Nevertheless, both electrode reactions result in a consumption of 2 F/mole of water. Up to the present, the Keidel cell has only been used rarely in the way described here. The use of this cell will be referred to again later.

#### AUTOMATION. CONTINUOUS ANALYSIS OF PROCESS STREAMS

Automation of the coulometric methods discussed involves no difficulties at the present time. Rather, it would be better to say that automatic potentiometric, amperometric, or photometric titrations have been fully electrified instead of partly mechanized<sup>227,228</sup>, as was the case previously. The titration is terminated by automatic cut-off of the generating current. In this context, attention may be drawn to the importance of a modification which makes a cautious approach to the end-point (anticipation circuit<sup>229-232</sup>) possible. There is not yet any question of complete automation because several discontinuous operations remain, such as the supply of samples, the discharge of the contents of the titration vessel after a determination, and the rinsing of the vessel. It is only with cumbersome equipment that the cycle can be repeated automatically in its entirety<sup>233,234</sup>.

The demand for continuous control of process streams (gases as well as liquids) has given rise to devices which furnish uninterrupted information, in a much simpler way. This would almost amount to a contradiction, if it were not for the fact that the quality of the information (*i.e.* its accuracy) is inferior to that which can be obtained with the discontinuously conducted galvanostatic methods. Nevertheless, the accuracy is amply sufficient for checking purposes.

The relation between the current intensity  $i$  (in ampères), the concentration  $C$ , and the flow rate  $r$  of the sample (in moles/l and l/sec, respectively) can easily be derived if the effect of the response time is ignored. The number of moles supplied per sec is  $Cr$ , which corresponds to  $nCr$  electrochemical equivalents. Every equivalent demands  $F$  coulombs. The number of coulombs required per second is thus  $nrCF$ , which is therefore equal to the current intensity  $i$ .

In continuous analysis, two principles may again be distinguished: (1), methods in which the potential is controlled; (2), methods in which the current intensity is controlled, which may imply that: (a), the current intensity is completely constant, so that the apparatus has to regulate the feeding rate of the gas or the liquid in such a way that it is always inversely proportional to the content; or (b), the feeding rate of the sample is completely constant, the monitoring device ensuring that the current intensity is always proportional to the content.

#### 1. Potentiostatic methods

*Sample flow constant.* As far as is known, only ECKFELDT<sup>235</sup> has described a method in which the potential of the working electrode is kept constant as effectively as possible with a (electro-mechanical) potentiostat. In the other methods the potential (sometimes the terminal voltage) is only approximately constant.

As previously described, in the discontinuous potentiostatic method, completeness is approached asymptotically. For the continuous method this means that the sample has to move along the working electrode *via* as long a path as possible. The electrode

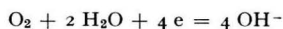


compartment and the working electrode are, therefore, constructed in such a way that the electrolyte flows along the electrode in a very thin layer *via* a labyrinthine path. For complete reaction, with this form of electrode, a minimum transit time of about 1 min seemed necessary. Communication with the space in which the comparison electrode is located is made *via* a porous disc. The generating current is recorded, and is proportional to the concentration. The difficulty of constructing a good working electrode is offset here by the advantage that the electric circuit is very simple, because it is exclusively the potentiostat which governs the process; control is not achieved *via* a signal from an indicating electrode, so that an indicator circuit is superfluous. With this method, determinations of iodide, of iodine, and of dissolved oxygen have been tested.

The next example to be discussed is the determination of oxygen according to HERSCH<sup>236-239</sup>. The oxygen-containing gas flows past a silver gauze electrode, slightly moistened with 5 N KOH. Separated from this electrode by a layer of porous plastic is the auxiliary electrode, for which HERSCH chose lead. The anode (Pb) and cathode (Ag) are connected *via* a resistor; the voltage drop across this resistor is recorded on a normal millivolt recorder. The electrode reactions are:



and



Owing to an accidental feature, therefore, internal electrolysis can be used in this case. The reaction in the Hersch cell, however, is not complete and hence the necessity of plotting a calibration graph arises. The problem of preparing gas samples of known composition has been solved in a very elegant way. Nitrogen thoroughly freed from oxygen (by means of a Pd-H<sub>2</sub> catalyst) is passed through a micro oxy-hydrogen coulometer, and subsequently through the Hersch cell. Control of the current intensity by means of the oxy-hydrogen coulometer makes it possible to adjust the oxygen content of the constant stream of nitrogen as desired. This content then corresponds to the deflection of the millivolt meter.

The measuring range is from 0.1-30 p.p.m., with a relative accuracy to within about 1%. Higher contents can also be determined by diluting the sample, which can be done in a simple way<sup>2,238</sup>. Indirect determination of traces of hydrogen is also possible by means of this cell<sup>236,239</sup>.

Recently KEIDEL<sup>240</sup> achieved complete conversion of the oxygen by providing better contact between the oxygen and the cathode, and at the same time, better convection of the electrolyte. For this purpose, he uses a porous silver electrode, through which the gas sample is passed, *i.e.* through a gas washing bottle fitted with a sintered-glass disc. For determinations in carbon dioxide, the potassium hydroxide can be replaced by potassium hydrogen carbonate<sup>241</sup>.

If a determination in solution is necessary, oxygen may be removed by stripping, using an oxygen-free gas stream<sup>238,240</sup>.

The last example to be discussed is the continuous determination of water in gases with Keidel's coulometric hygrometer<sup>225,242-244</sup>, discussed above, which has been adopted mainly for such applications.

The cell is connected to a 75-100 V battery *via* a resistor of 1000  $\Omega$  and a microam-

père meter or a recorder (the method is only approximately potentiostatic). A water content of 1 p.p.m. (v/v) corresponds to a current of 13.4  $\mu\text{A}$ . The hygrometer has a range of 1–2000 p.p.m. The lower limit is fixed by the intensity of the residual current.

This method can also be employed for individual analyses<sup>245</sup>. This merely involves the integration of the current–time function. A particularly interesting application is in elementary analysis<sup>226</sup>, where the galvanostatic method is also applicable.

## 2. Control of the current

In the two cases falling under this heading, the control mechanism is based on the feed-back principle. The difference between the actual indicator signal at any time and its desired value is amplified and used for correcting any deviation from the previously fixed degree of advancement of the reaction.

The comparison value of the potential or of the current intensity, using potentiometric or amperometric indication, does not always coincide with the value that may be expected for a complete reaction. It is often advantageous for a constant excess of the generated reagent to be present at the point where the sample stream leaves the electrolytic cell. For gases this procedure involves no systematic error (apart from a few moments after control is started), but it does reduce the risk of losses. From the above statement it can be inferred that, in general, the presence of an auxiliary substance is required in this method. The sample first moves along the working electrode, and then along the electrodes of the indicating system. The auxiliary electrode is located behind a sintered-glass disc. The design of the electrolytic cell does not entail — in contrast with ECKFELDT's potentiostatic method<sup>235</sup> — that the potential difference between the working electrode and the adjacent liquid be uniform along the electrode surface. In the case of gaseous substances, the supporting electrolyte with auxiliary substance can be used for a long, if not unrestricted, time; with liquid samples they have to be renewed continuously. This does not present any difficulties.

*2a. Constant generating current, sample flow monitored by the indicator circuit.* In this method, which up to the present has probably been described only in the patent granted to ECKFELDT<sup>246</sup>, the indicator signal influences the position of a throttling valve in the sample stream. The setting of a flow meter, which is recorded, indicates the concentration.

*2b. Generating current monitored by the indicator circuit, constant sample flow rate*<sup>247,248</sup>. Here, the indicating system regulates the magnitude of the generating current, which is recorded. This class includes the oldest continuous coulometric method, *viz.* control of the mustard gas content of the air<sup>249</sup>. The apparatus is also suitable for hydrogen sulphide, thiophene and mercaptans, in very low concentrations (0.5 p.p.m.)<sup>248,250,251</sup>. Other determinations are those of borane<sup>252</sup>, ozone<sup>253</sup>, water<sup>254</sup> chlorine<sup>255</sup>, halide ions<sup>256</sup>, copper<sup>257</sup>, bases<sup>258</sup> and sulphur dioxide<sup>248,259</sup>.

By inserting a current–time integrator, the same apparatus can be used in some discontinuous methods. LIBERTI has elaborated this idea in gas chromatography<sup>260–263</sup>. The eluted compounds are combusted by passing them over heated copper(II) oxide (when necessary, additional oxygen can be supplied). Subsequently, the carbon dioxide is absorbed in the titration cell and titrated simultaneously. Organic compounds containing halogens or sulfur have been determined by COULSON<sup>263a</sup>

after reduction or oxidation. Probably the high gas velocity prevents the very important coulometric analysis of carbon, sulphur and oxygen in steel<sup>264,265</sup> from being carried out in the same way. Here, absorption takes place in a slightly alkaline solution, which is titrated afterwards. A similar procedure is also followed in elementary analysis<sup>266</sup>.

## SUMMARY

Coulometry has developed in different ways, and has become a very accurate analytical tool, even when applied in trace analysis. The theoretical interpretations of various cases encountered in amperostatic coulometry, and the principles underlying continuous process control, are stressed.

A nearly complete literature survey covering the determination of the thickness of surface layers is given.

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## CURRENT SCANNING POLAROGRAPHY AT THE DROPPING MERCURY ELECTRODE

TAITIRO FUJINAGA AND KOSUKE IZUTSU

*Chemistry Institute, Faculty of Science, University of Kyoto (Japan)*

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### INTRODUCTION

Polarography at controlled current with the dropping mercury electrode (D.M.E.) as the indicator electrode was first introduced by ISHIBASHI AND FUJINAGA<sup>1</sup> in 1956. In this method the current flowing through the D.M.E. is controlled by the external current source, and the potential of the D.M.E. is measured against a reference electrode such as the S.C.E. The applied current-potential curve, which is obtained by recording the potential at the end of the drop life against the applied current, has an almost identical shape to that of the conventional polarogram. This method was investigated theoretically by SENDA *et al.*<sup>2</sup> by solving the ILKOVIĆ differential equation. They concluded that the limiting current in this method is expressed by:

$$i_l = 635nD^{1/2}C^*m^{2/3}t_{max}^{1/6}$$

KOLTHOFF *et al.*<sup>3</sup> also investigated this method in detail. They found that the limiting current is influenced by the electrode reaction of the substance which is reduced at more negative potentials, or by the second constituent. According to them, the limiting current is equal to:

$$i_l = 708nD^{1/2}C^*m^{2/3}t_{max}^{1/6}$$

when the reduction of the second constituent is totally irreversible, although it becomes smaller, owing to the re-oxidation current of the second constituent when it is reduced reversibly.

In the present paper theoretical fundamentals were studied, in order to make this method applicable for analytical purposes. The equations for the current-potential curve, and also for the limiting current, were derived by taking into account the reversibility of the electrode process of the substance reduced at more negative potentials. The theoretical results were found to be in good agreement with the results obtained experimentally for typical examples.

### THEORETICAL

#### *Potential-time relations for the D.M.E.*

The electrolytic solution containing three reducible substances  $O_1$ ,  $O_2$  and  $O_s$  is considered. They are reduced at the D.M.E., and the products of the reduction,  $R_1$ ,  $R_2$  and  $R_s$ , are soluble either in water or in mercury. The concentration and the standard potential of the reducible species are shown by  $C^*_{o_1}$ ,  $C^*_{o_2}$ ,  $C^*_{o_s}$  and  $E^{\circ}_1$ ,  $E^{\circ}_2$ ,  $E^{\circ}_s$ ,

respectively. Here  $E^{\circ}_1 \gg E^{\circ}_2 \gg E^{\circ}_s$  and  $C^*_{O_1}, C^*_{O_2} \ll C^*_{O_s}$ . Species  $O_s$  which is present in high concentration ( $\gtrsim 0.1 M$ ) acts as the supporting electrolyte. During the life of the D.M.E. the applied current is maintained constant ( $i_0$ ). The concentration of each species can be calculated by solving the ILKOVIČ differential equation (1) under proper conditions.

$$\frac{\partial C_j(x,t)}{\partial t} = D_j \frac{\partial^2 C_j(x,t)}{\partial x^2} + \frac{2x}{3t} \cdot \frac{\partial C_j(x,t)}{\partial x} \quad (1)$$

where  $j$  represents  $O_1, O_2, O_s, R_1, R_2$  and  $R_s$ ,  $C_j(x,t)$  represents the concentration ( $mM$ ),  $D_j$  represents the diffusion coefficient ( $cm^2/sec$ )  $x$  is the distance from the electrode surface ( $cm$ ),  $t$  is the time (in sec) since the drop began to form. The electrode area at  $t=0$  was assumed to be zero. The migration and charging effects are neglected here.

### 1. Potential-time relations at $0 \leq t \leq \tau_{s \rightarrow 2} \dagger$

Because the electrode area is very small at the beginning of the drop life, the sum of the diffusion currents due to the reductions of  $O_1$  and  $O_2$  is not sufficiently large to consume the applied current  $i_0$ . Therefore, simultaneous reduction of  $O_s$  is necessary, and the potential becomes very negative. The concentrations of  $O_1, O_2, R_1$  and  $R_2$ , and the reduction currents of  $O_1$  and  $O_2$  can be calculated using the condition:  $C_{O_p}(0,t) = 0$  ( $p = 1, 2$ ). The results are as follows:

$$C_{O_p}(x,t) = C^*_{O_p} \operatorname{erf} \left( \sqrt{\frac{7}{3}} \frac{x}{2 D_{O_p}^{1/2} t^{1/2}} \right) \quad (2)$$

$$C_{R_p}(x,t) = \sqrt{\frac{D_{O_p}}{D_{R_p}}} C^*_{O_p} \operatorname{erfc} \left( \sqrt{\frac{7}{3}} \frac{x}{2 D_{R_p}^{1/2} t^{1/2}} \right) \quad (3)$$

$$i_p = 708 n_p D_{O_p}^{1/2} C^*_{O_p} m^{2/3} t^{1/6} \quad (4)$$

where  $i_p$  is measured in  $\mu A$ . Equation (4) is the same as for the instantaneous diffusion current in conventional polarography (ILKOVIČ equation).

The concentration distributions of  $O_s$  and  $R_s$  can be calculated by solving eqn. (1) under the initial condition:  $C_{O_s}(x,0) = C^*_{O_s}$ , and the boundary condition:  $i_s = i_0 - (i_1 + i_2)$ , where  $i_s$  is the reduction current of  $O_s$ . The results are:

$$C_{O_s}(z,y) = C^*_{O_s} + \frac{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p}}{n_s D_{O_s}^{1/2}} \operatorname{erf} \left( \frac{z}{2 D_{O_s}^{1/2} y^{1/2}} \right) - \left( \frac{3}{7} \right)^{4/7} \frac{i_0}{n_s F \beta D_{O_s}^{1/2}} \int_0^y \frac{(y-S)^{-4/7}}{\sqrt{\pi S}} \exp \left( -\frac{z^2}{4 D_{O_s} S} \right) dS \quad (5)$$

$$C_{R_s}(z,y) = \left( \frac{3}{7} \right)^{4/7} \frac{i_0}{n_s F \beta D_{R_s}^{1/2}} \int_0^y \frac{(y-S)^{-4/7}}{\sqrt{\pi S}} \exp \left( -\frac{z^2}{4 D_{R_s} S} \right) dS - \frac{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p}}{n_s D_{R_s}^{1/2}} \operatorname{erf} \left( \frac{z}{2 D_{R_s}^{1/2} y^{1/2}} \right) \quad (6)$$

†  $\tau_{s \rightarrow 2}$  is the time when the potential of the D.M.E. shifts abruptly to a positive direction from the reduction potential of  $O_s$ .

with

$$y = \frac{3}{7} t^{7/3}, \quad z = xt^{2/3}, \quad \beta = 0.008515 m^{2/3}, \quad 0 \leq t \leq (\tau_{s \rightarrow 2})'$$

From eqns. (5) and (6), the surface concentrations of  $O_s$  and  $R_s$  can be written as:

$$C_{O_s}(0,t) = C^*_{O_s} - \frac{i_0}{635 n_s D_{O_s}^{1/2} m^{2/3} t^{1/6}} + \frac{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p}}{n_s D_{O_s}^{1/2}} \quad (7a)$$

$$C_{R_s}(0,t) = \sqrt{\frac{D_{O_s}}{D_{R_s}}} (C^*_{O_s} - C_{O_s}(0,t)) \quad (7b)$$

where

$$96500 \cdot 0.008515 \cdot \sqrt{\frac{7}{3}} \cdot \Gamma\left(\frac{13}{14}\right) / \Gamma\left(\frac{3}{7}\right) = 635$$

As  $C_{O_1}(0,t)$  and  $C_{O_2}(0,t)$  are zero for  $0 \leq t \leq \tau_{s \rightarrow 2}$ , the potential of the D.M.E. is controlled by  $C_{O_s}(0,t)$  and  $C_{R_s}(0,t)$ . According to the absolute rate theory, the relation between the potential and the surface concentrations of  $O_s$  and  $R_s$  can be written, assuming a first-order reaction, as:

$$i_s = \beta t^{2/3} n_s F \left[ \overset{\rightarrow}{k}_s C_{O_s}(0,t) \exp\left(-\frac{\alpha_s n'_s F}{RT} E\right) - \overset{\leftarrow}{k}_s C_{R_s}(0,t) \exp\left\{\frac{(1 - \alpha_s) n'_s F}{RT} E\right\} \right] \quad (8)$$

in which  $\alpha_s$  is the transfer coefficient for the electrode process  $O_s + n_s e = R_s$ ,  $n_s$  is the number of electrons involved, and  $\overset{\rightarrow}{k}_s$ ,  $\overset{\leftarrow}{k}_s$  are the rate constants of oxidation and reduction at  $E = 0$ . The transition time  $(\tau_{s \rightarrow 2})'$ , when the potential of the D.M.E. shifts abruptly toward more anodic values until it is controlled by the system of  $O_2$ , varies according to the reversibility of the electrode process of  $O_s$ .

(i) When the reduction of  $O_s$  is reversible, the potential is calculated from the NERNST equation instead of from eqn. (8). The transition time  $(\tau_{s \rightarrow 2})_{Rev}$  is determined by the condition:  $C_{R_2}(0,t) = 0$ , i.e., in view of eqn. (7), by the eqn.:

$$(\tau_{s \rightarrow 2})_{Rev} = (i_0/635 \sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p} m^{2/3})^6 \quad (9)$$

(ii) When the reduction of  $O_s$  is totally irreversible†, the second term in parenthesis on the right hand of eqn. (8) can be neglected. The potential shifts towards a more anodic direction when  $i_s$  becomes zero. From eqn. (4),

$$(\tau_{s \rightarrow 2})_{Irr} = (i_0/708 \sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p} m^{2/3})^6 \quad (10)$$

(iii) When the re-oxidation of  $R_s$  proceeds at potentials between the reduction potentials of  $O_s$  and  $O_2$ , the potential decreases stepwise towards the reduction potential of  $O_2$ . The transition times are  $(\tau_{s \rightarrow 2})_{Irr}$  and  $(\tau_{s \rightarrow 2})_{Rev}$ , respectively. The diagram shown in Fig. 1 explains the nature of the potential-time curve qualitatively.

† In this paper, when the reduction of  $O_p$  is totally or completely irreversible, the reduced form  $R_p$  is not re-oxidized at the potential at which the reduction of  $O_1$  occurs.

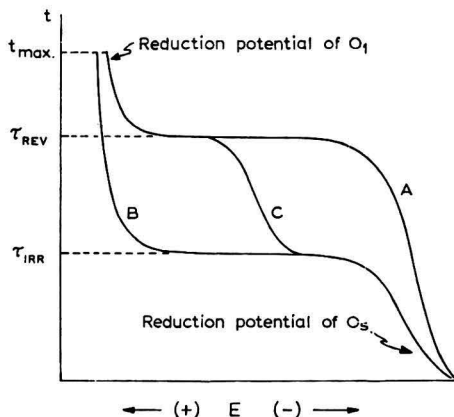
2. Potential-time relations at  $(\tau_{s \rightarrow 2}) \leq t \leq (\tau_{2 \rightarrow 1})$ (A) Surface concentrations of  $O_2$  and  $R_2$ .(1) When the reaction process of  $O_s$  is reversible, the current due to the re-oxidation of

Fig. 1. Potential-time curves of the solution containing  $O_1$  and  $O_s$  ( $O_2$  absent). The reduction processes of  $O_s$  are A, reversible, B, totally irreversible, and C, irreversible, but  $R_s$  is re-oxidized at the potential between the reduction potentials of  $O_1$  and  $O_s$ .

$R_s$  must be taken into account even after the transition time  $(\tau_{s \rightarrow 2})_{Rev}$ . This re-oxidation current of  $R_s$  can be calculated by solving eqn. (1). The initial condition is the concentration of  $R_s$  for  $t = (\tau_{s \rightarrow 2})_{Rev}$ , while the boundary condition is that  $C_{R_s}(0, t) = 0$  after  $(\tau_{s \rightarrow 2})_{Rev}$ . Thus the current  $i_s$  at  $(\tau_{s \rightarrow 2})_{Rev} \leq t \leq \tau_{2 \rightarrow 1}$  is given by:

$$i_s = i_0 \{y' + (y_{s \rightarrow 2})_{Rev}\}^{4/7} \int_0^{(y_{s \rightarrow 2})_{Rev}} \{(y_{s \rightarrow 2})_{Rev} - S\}^{-4/7} \frac{\sqrt{y'}}{\pi \sqrt{S(S+y')}} dS - \left(\frac{7}{3}\right)^{4/7} \frac{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p} F \beta}{\pi^{1/2}} \{y' + (y_{s \rightarrow 2})_{Rev}\}^{11/4} \quad (11)$$

where

$$y' = \frac{3}{7} \{t^{7/3} - (\tau_{s \rightarrow 2})_{Rev}^{7/3}\} \quad \text{and} \quad (y_{s \rightarrow 2})_{Rev} = \frac{3}{7} (\tau_{s \rightarrow 2})_{Rev}^{7/3}$$

The surface concentrations of  $O_2$  and  $R_2$  can be derived by considering their concentrations for  $t = (\tau_{s \rightarrow 2})_{Rev}$  as the initial condition and the current  $i_2$  equal to  $i_0 - (i_1 + i_s)$  as the boundary condition. Thus,

$$C_{O_2}(0, t) = C^*_{O_2} + \frac{n_1 D_{O_1}^{1/2} C^*_{O_1}}{n_2 D_{O_2}^{1/2}} - \frac{i_0}{635 n_2 D_{O_2}^{1/2} m^{2/3} t^{1/6}} \quad (12a)$$

$$C_{R_2}(0, t) = \sqrt{\frac{D_{O_2}}{D_{R_2}}} (C^*_{O_2} - C_{O_2}(0, t)) \quad (12b)$$

(2) When the reduction of  $O_s$  is completely irreversible,  $i_s$  is zero after  $(\tau_{s \rightarrow 2})_{Irr}$ .

From this, eqns. (13a) and (13b) are obtained as the surface concentrations of  $O_2$  and  $R_2$  at  $(\tau_{s \rightarrow 2})_{Irr} \leq t \leq \tau_{2 \rightarrow 1}$ .

$$C_{O_2}(o, y'') = \frac{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p}}{n_2 D_{O_2}^{1/2}} \cdot P - \left(\frac{3}{7}\right)^{4/7} \frac{i_0}{\pi^{1/2} n_2 F \beta D_{O_2}^{1/2}} [(y_{s \rightarrow 2})_{Irr} + y'']^{1/14} \cdot Q \quad (13a)$$

$$C_{R_2}(o, y'') = \sqrt{\frac{D_{O_2}}{D_{R_2}}} [C^*_{O_2} - C_{O_2}(o, y'')] \quad (13b)$$

where

$$P = \frac{2}{\pi} \sin^{-1} \sqrt{1 - z''}, \quad Q = \int_{z''}^1 \theta^{-4/7} (1 - \theta)^{-1/2} d\theta, \quad z'' = (y_{s \rightarrow 2})_{Irr} / \{y'' + (y_{s \rightarrow 2})_{Irr}\},$$

$$(y_{s \rightarrow 2})_{Irr} = \frac{3}{7} (\tau_{s \rightarrow 2})_{Irr}^{7/3}, \quad \text{and} \quad y'' = \frac{3}{7} \{t^{7/3} - (\tau_{s \rightarrow 2})_{Irr}^{7/3}\}.$$

(B) *Potential-time relations.* The potential is controlled at this stage by the system of  $O_2$ , namely, by  $C_{O_2}(o, t)$  and  $C_{R_2}(o, t)$ . Eqn. (14) represents the relation between the potential and the surface concentrations of  $O_2$  and  $R_2$ .

$$i_2 = n_2 \beta F t^{2/3} \left\{ \overset{\rightarrow}{k_2} C_{O_2}(o, t) \exp\left(-\frac{\alpha_2 n'_2 F}{RT} E\right) - \overset{\leftarrow}{k_2} C_{R_2}(o, t) \exp\left(\frac{(1 - \alpha_2) n'_2 F}{RT} E\right) \right\} \quad (14)$$

Here, the transition of the potential towards the reduction potential of  $O_1$  occurs at different times according to the electrode processes of  $O_s$  and  $O_2$ .

(i) When  $O_2$  and  $O_s$  are both reduced reversibly, the NERNST equation is valid.  $\tau_{2 \rightarrow 1}$  is obtained from eqn. (12) at the time when  $C_{R_2}(o, t)$  becomes zero.

$$\tau_{2 \rightarrow 1} = [i_0 / 635 n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3}]^6 \quad (15)$$

(ii) When both of the reductions of  $O_2$  and  $O_s$  are totally irreversible,  $\tau_{2 \rightarrow 1}$  is the time at which  $i_1$  becomes equal to  $i_0$ . From eqn. (4),

$$\tau_{2 \rightarrow 1} = [i_0 / 708 n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3}]^6 \quad (16)$$

(iii) When the reduction of  $O_s$  is reversible and that of  $O_2$  is totally irreversible,  $\tau_{2 \rightarrow 1}$  is the time at which  $i_2$  becomes zero. By taking the current due to the re-oxidation of  $R_s$  into account, the following relation is obtained for  $t = \tau_{2 \rightarrow 1}$ .

$$\begin{aligned} \frac{1}{\pi^{1/2}} (1 + z')^{1/2} \int_0^1 (1 - \theta)^{-4/7} \theta^{-1/2} (1 + z' \theta)^{-1} d\theta - \pi^{1/2} \frac{(\tau_{s \rightarrow 2})_{Rev}^{1/6}}{(\tau_{2 \rightarrow 1})^{1/6}} \\ = \frac{\Gamma\left(\frac{3}{7}\right)}{\Gamma\left(\frac{13}{14}\right)} \cdot \frac{n_2 D_{O_2}^{1/2} C^*_{O_2}}{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p}} \end{aligned} \quad (17)$$

where

$$z' = (\tau_{s \rightarrow 2})_{Rev}^{7/3} / \{\tau_{2 \rightarrow 1}^{7/3} - (\tau_{s \rightarrow 2})_{Rev}^{7/3}\}.$$

In Table I the values of  $\tau_{2 \rightarrow 1} / (\tau_{s \rightarrow 2})_{Rev}$  are calculated as a function of  $K = n_2 D_{O_2}^{1/2} C^*_{O_2} / n_1 D_{O_1}^{1/2} C^*_{O_1}$  from eqn. (17).

TABLE I

THE EFFECT OF  $O_2$  ON THE LIMITING CURRENT OF  $O_1$ : THE REDUCTION OF  $O_s$  IS REVERSIBLE, WHILE THAT OF  $O_2$  IS TOTALLY IRREVERSIBLE

$K$	$\tau_{2 \rightarrow 1} / (\tau_{s \rightarrow 2})_{Rev}$	$X$
0	1	635.0
0.01447	1.00427	643.7
0.02519	1.0127	649.6
0.04630	1.0470	659.9
0.07975	1.1119	672.9
0.1390	1.346	688.3
0.2230	1.875	699.4
0.3166	2.795	704.4
0.4326	4.552	706.7
0.5492	7.227	707.5
0.8257	19.315	707.7
$\infty$	$\infty$	708.0

(iv) When the reaction of  $O_s$  is totally irreversible, and that of  $O_2$  is reversible, the potential shifts to the more anodic potential when  $C_{R_2}(0,t)$  becomes zero. From eqn. (13) the following relation is obtained at the transition time  $\tau_{2 \rightarrow 1}$ :

$$\frac{2}{\pi} \sin^{-1} \sqrt{1 - z''} - \frac{z''^{1/14}}{\pi} \int_{z''}^1 \theta^{-4/7} (1 - \theta)^{-1/2} d\theta = \frac{n_2 D_{O_2}^{1/2} C^*_{O_2}}{\sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p}} \quad (18)$$

where  $z'' = (y_{s \rightarrow 2})_{Irr} / \{y'' + (y_{s \rightarrow 2})_{Irr}\}$ . From this equation,  $\tau_{2 \rightarrow 1}$  was calculated as a function of  $K$  (Table II).

TABLE II

THE EFFECT OF  $O_2$  ON THE LIMITING CURRENT OF  $O_1$ : THE REDUCTION OF  $O_s$  IS TOTALLY IRREVERSIBLE WHILE THAT OF  $O_2$  IS REVERSIBLE

$K$	$(\tau_{s \rightarrow 2})_{Irr} / \tau_{2 \rightarrow 1}$	$X$
0	1	708.0
0.0166	0.7430	685.0
0.0472	0.5520	671.5
0.0975	0.3728	659.2
0.1768	0.2225	648.4
0.2634	0.1390	643.8
0.4769	0.05180	638.4
0.7361	0.01939	636.8
1.043	0.007197	635.7
3.647	0.00005180	635.2
$\infty$	0	635.0

3. *Potential-time relations where the concentration of  $O_2$  in the bulk of the solution is equal to zero.*

In this case, the surface concentration of  $O_1$  and  $R_1$  after the transition time  $\tau_{s \rightarrow 1}$  can be calculated. If the reduction of  $O_s$  is reversible,

$$C_{O_1}(0,t) = C^*_{O_1} - \frac{i_0}{635n_1 D_{O_1}^{1/2} m^{2/3} t^{1/6}} \quad (19a)$$

$$C_{R_1}(0,t) = \frac{i_0}{635n_1 D_{O_1}^{1/2} m^{2/3} t^{1/6}} \quad (19b)$$

but when  $O_s$  is reduced totally irreversibly,

$$C_{O_1}(o,t) = AC^*_{O_1} - \frac{Bi_0}{n_1 D_{O_1}^{1/2} m^{2/3} t^{1/6}} \quad (20a)$$

$$C_{R_1}(o,t) = \sqrt{\frac{D_{O_1}}{D_{R_1}}} [C^*_{O_1} - C_{O_1}(o,t)] \quad (20b)$$

where

$$A = \frac{2}{\pi} \sin^{-1} \sqrt{1 - \nu^{7/3}}, \quad B = \sqrt{\frac{3}{7}} \frac{1}{821.7\pi^{1/2}} \int_0^1 \theta^{-4/7} (1 - \theta)^{-1/2} d\theta, \quad \nu = (\tau_{s \rightarrow 1})_{irr}/t$$

By applying the NERNST equation, one can obtain the equations for the potential-time curves (Fig. 1).

### Current-potential curves and their limiting currents

The current-potential curve ( $E_{max}$ - $i$  curve) in this method is obtained, as mentioned already, by plotting the potential at the end of the drop life, ( $E_{max}$ ), against the applied current.

(I) In the absence of the species  $O_2$ , the equations for  $i$ - $E_{max}$  curves of  $O_1$  can be derived from eqn. (19) or (20) and the NERNST equation. For simplicity, only the case in which  $O_1$  is reduced reversibly is considered here.

(i) When the reduction of  $O_s$  (supporting electrolyte) occurs reversibly, from eqn. (19) and the NERNST equation we obtain eqns. (21a) and (21b)

$$E_{max} = (E_{\frac{1}{2}})_{O_1} - \frac{RT}{n_1 F} \ln \frac{i}{(i)_{rev} - i} \quad (21a)$$

$$(i)_{rev} = 635 n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3} t_{max}^{1/6} \quad (21b)$$

This equation has the identical form as that for the conventional polarogram, except that the constant of the limiting current differs from that of the diffusion current. The polarogram has a current plateau, as shown in Fig. 2, curve A, whose height is in

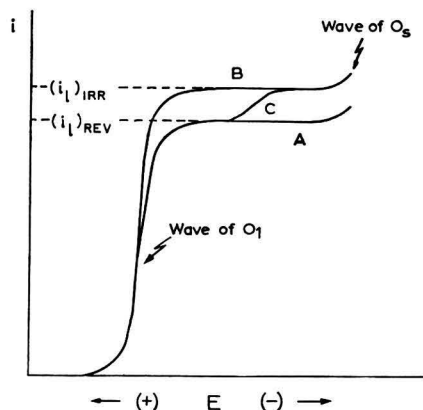


Fig. 2. Current-potential curves of the solution containing  $O_1$  and  $O_s$  ( $O_2$  absent). A, B and C correspond to those in Fig. 1.

the ratio 635 : 708 to that of the maximum diffusion current. The potential at which



$i = \frac{1}{2}(i)_{Rev}$  is equal to the half-wave potential  $(E_{\frac{1}{2}})_{O_1}$  in the conventional method.  
 (ii) When the reduction of  $O_s$  is totally irreversible, the  $i-E_{max}$  curve, from eqn. (20) and the NERNST equation, is given by,

$$E_{max} = (E_{\frac{1}{2}})_{O_1} - \frac{RT}{n_1 F} \ln \frac{(1 - A_{max})C^*_{O_1} + B_{max}i/n_1 D_{O_1}^{1/2} m^{2/3} t_{max}^{1/6}}{A_{max}C^*_{O_1} - B_{max}i/n_1 D_{O_1}^{1/2} m^{2/3} t_{max}^{1/6}} \quad (22a)$$

$$(i)_{Irr} = 708n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3} t_{max}^{1/6} \quad (22b)$$

where  $A_{max}$  and  $B_{max}$  are the values of  $A$  and  $B$  for  $t_{max}$ . The limiting current is equal to the maximum diffusion current (Fig. 2, curve B). The potential at which  $i = \frac{1}{2}(i)_{Irr}$  can be written approximately by,

$$E_{max} = (E_{\frac{1}{2}})_{O_1} - 0.0057/n_1$$

where  $E_{max}$  is measured in V at 25°. This value is only a few mV more negative than that of the conventional half-wave potential, as was demonstrated experimentally by ISHIBASHI AND FUJINAGA<sup>1</sup>.

(iii) When the re-oxidation of  $R_s$  occurs between the reduction potentials of  $O_1$  and  $O_s$ , the current-potential curve has the shape as shown in Fig. 2, curve C. It was noteworthy that a small second wave (the height of which is equal to  $(i)_{Irr} - (i)_{Rev}$ ) appears at the re-oxidation potential of  $R_s$ , which cannot be observed in the conventional polarogram.

(2) When the species  $O_2$  co-exists, it is difficult to obtain the equations for the surface concentrations of  $O_1$  and  $R_1$  after the transition time  $\tau_{s \rightarrow 1}$ . Therefore, only the limiting current of  $O_1$  is considered here.

(i) When the reductions of  $O_2$  and  $O_s$  are reversible, the limiting current of  $O_1$  is obtained from eqn. (15). The limiting current is equal to the applied current for the case when  $\tau_{2 \rightarrow 1}$  is equal to  $t_{max}$ .

$$(i)_{Rev} = 635n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3} t_{max}^{1/6} \quad (21b)$$

(ii) When both  $O_2$  and  $O_s$  are reduced completely irreversibly,  $i_l$  is, from eqn. (16),

$$(i)_{Irr} = 708n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3} t_{max}^{1/6} \quad (22b)$$

(iii) When the reduction of  $O_s$  is reversible, but that of  $O_2$  is totally irreversible, the limiting current of  $O_1$  increases with the increase of the concentration of  $O_2$ . From eqn. (15),

$$\begin{aligned} i_0 &= 635 \sum_{p=1,2} n_p D_{O_p}^{1/2} C^*_{O_p} m^{2/3} (\tau_{s \rightarrow 2})_{Rev}^{1/6} \\ &= 635(1 + K) \left\{ \frac{(\tau_{s \rightarrow 2})_{Rev}}{\tau_{2 \rightarrow 1}} \right\}^{1/6} n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3} (\tau_{2 \rightarrow 1})^{1/6} \end{aligned} \quad (23)$$

If the limiting current of  $O_1$  is expressed by  $i_l = X n_1 D_{O_1}^{1/2} C^*_{O_1} m^{2/3} t_{max}^{1/6}$ ,  $X$  can be evaluated by,

$$X = 635(1 + K) \left\{ \frac{(\tau_{s \rightarrow 2})_{Rev}}{t_{max}} \right\}^{1/6}$$

and the values are shown in Table I and in Fig. 3, curve A. With increase of  $K$ ,  $X$

is increased and converges towards 708. When  $K$  is larger than 0.5,  $X$  may be regarded as 708, independently of the concentration of the species  $O_2$ .

(iv) When the reduction of  $O_s$  is totally irreversible, but that of  $O_2$  is reversible, the limiting current of  $O_1$  changes with the concentration of  $O_2$ . In this case,

$$X = 708(1 + K) \left\{ \frac{(\tau_{s \rightarrow 2})_{irr}}{t_{max}} \right\}^{1/6}$$

the value of  $X$  is as shown in Table II and Fig. 3, curve B.

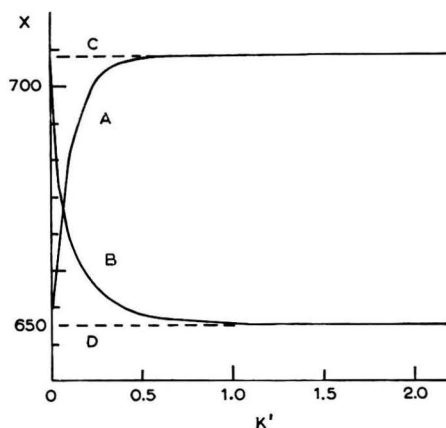


Fig. 3. Variation of  $X$  with  $K$ : A, reduction of  $O_s$  reversible, reduction of  $O_2$  irreversible; B, reduction of  $O_s$  irreversible, reduction of  $O_2$  reversible; C, reduction of  $O_s$  irreversible, reduction of  $O_2$  irreversible; D, reduction of  $O_s$  reversible, reduction of  $O_2$  reversible.

From these results one can conclude that if the concentration of  $O_2$  is sufficiently large to fulfil the condition  $K > 0.5$ , the limiting current of  $O_1$  may be considered to be determined by the reversibility of the electrode reaction of  $O_2$ , although the diffusion coefficient of  $O_1$  is determined by all the components present.

#### APPARATUS AND REAGENTS

Figure 4 shows a schematic circuit of the equipment for the automatic recording of current-scan polarograms. With the exception of the source for the linear variation of current with time, the system is comparable with that used in chronopotentiometry. A three-electrode system is employed, *i.e.*, the potential of the D.M.E. is measured

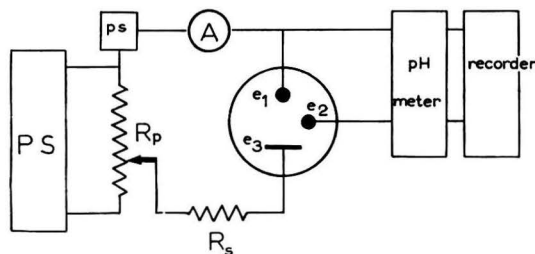


Fig. 4. Recording equipment: PS, power supply, 200 V regulated; ps, power supply for zero adjustment;  $R_p$ , 50 k $\Omega$  helipot, 10-turn;  $R_s$ , 1–50 M $\Omega$ ; A, microammeter;  $e_1$ , D.M.E.;  $e_2$ , S.C.E.;  $e_3$ , mercury pool or Pt plate electrode.

with respect to a reference S.C.E., through which no electrolysis current passes. In measuring the potential between the D.M.E. and S.C.E., a Shimadzu pH-meter, Model GM-1 was used as a preamplifier in the input circuit of the voltage recorder, Yanagimoto Polarorecorder.

The power supply PS has an output voltage of 200 V. The other power supply ps is used to adjust the current range applied from the cathodic to the anodic branch.  $R_p$  is a linearity helipot driven by a 1 rev/min synchronous motor, to provide the linear current output.  $R_s$  is a current-limiting large resistor. The microammeter, A, is used to check the current visually. The conventional polarograms were measured using a pen-and-ink recording polarograph (Shimadzu Pen Recording Polarograph RP-2 and Yanagimoto Polarorecorder), and also with a manual polarograph.

The characteristics of the electrode capillary were, for capillary A:  $m = 0.890$  mg sec<sup>-1</sup>,  $t = 4.0_0$  sec (open circuit),  $h = 69.4$  cm; and for capillary B:  $m = 0.850$  mg sec<sup>-1</sup>,  $t = 4.6_2$  sec (open circuit),  $h = 58.3$  cm (both in 1 M KNO<sub>3</sub> solution). All the measurements were made at  $25^\circ \pm 0.1^\circ$ .

All the reagents used were analytical grade. Unless otherwise mentioned, 0.01–0.02% polyacrylamide was added to the electrolytic solution.

#### EXPERIMENTAL RESULTS

As was shown in the theoretical treatment, the limiting current of this method is affected by the reversibility of the electrode processes of substances reduced at more negative potentials. When the concentration of the species  $O_2$  is large enough to fulfil the condition  $K > 0.5$ , the limiting current of  $O_1$  can be regarded as being determined by the reversibility of the reduction of  $O_2$ , although the diffusion current of the conventional method is changed little by the presence of  $O_2$ . (The diffusion coefficient is, of course, controlled by all the species present.) Therefore, the comparison of the limiting current of this method with that of the conventional method will serve as a method for testing the theoretical results. Considering these points, the effects of the substances reduced at the more negative potentials were investigated.

#### *The effect of large amounts of the substance reduced at more negative potentials*

Figure 5 shows current–potential curves for 0.97 mM Tl<sup>+</sup> in 1 M KNO<sub>3</sub>. Curves 1 and 1' were recorded in the presence of 2.0 mM Zn<sup>2+</sup> as  $O_2$ . This concentration is large compared with that of Tl<sup>+</sup>( $O_1$ ). Curve 1 is the current-scan polarogram, while 1' is the conventional polarogram recording the maximum current during the drop life. The limiting current of curve 1 is 3.25  $\mu$ A, while that of curve 1' is 3.71  $\mu$ A. This large difference in magnitude can be explained by the fact that Zn<sup>2+</sup> is reduced almost reversibly in this solution. Curves 2 and 2' show the polarograms of Tl<sup>+</sup> in the presence of Ni<sup>2+</sup> as  $O_2$ . The reduced form of Ni cannot be re-oxidized at the potential at which the reduction of Tl<sup>+</sup> occurs. In this case, the limiting currents of curves 2 and 2' are almost equal to each other, in good agreement with eqn. (22').

In Table III the limiting currents of this method are compared with the maximum diffusion current in the conventional method. In column (A) ( $O_2$  reversible), the value  $(708/635)i_l$  is in good agreement with the maximum diffusion current  $(i_a)_{max}$ . In column (B) ( $O_2$  totally irreversible),  $i_l$  itself has a value nearly equal to  $(i_a)_{max}$ .

For the case when the electrode process of the substance  $O_2$  reduced at the more negative potential is irreversible, and its reduced form is re-oxidized at a potential between

the reduction potentials of  $O_1$  and  $O_2$ , the current-potential curve will have a shape as shown in Fig. 2, curve C. This case occurs in the wave of  $Cd^{2+}$  when  $O_2$  is in excess is

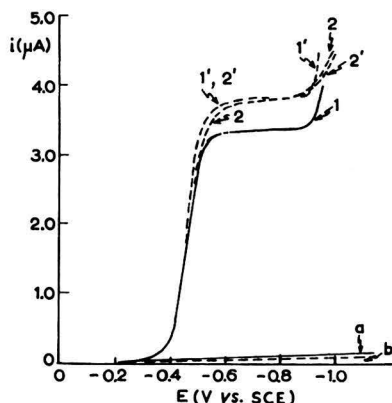


Fig. 5. Current-potential curves of  $Tl^+$  in  $KNO_3$  solution: 1 and 1', 0.975 mM  $Tl^+$ , 2.0 mM  $Zn^{2+}$ , 1 M  $KNO_3$ ; 2 and 2', 0.975 mM  $Tl^+$ , 2.0 mM  $Ni^{2+}$ , 1 M  $KNO_3$ ; a and b, 1 M  $KNO_3$  (capillary A). 1, 2 and a are the current scan polarograms and 1', 2' and b are the conventional polarograms (maximum current).

TABLE III

THE LIMITING CURRENT OF THE CURRENT SCANNING METHOD

	$O_1$ (mM)	$O_2$ (mM)	$O_s$ (M)	$i_l$ ( $\mu A$ )	$(708/635)i_l$ ( $\mu A$ )	$(i_l)_{max}$ ( $\mu A$ )
(A)	$Tl$ 0.975	$Zn$ 2.0	$KNO_3$ 1	3.30	3.68	3.71
$O_2$ reversible	$Cd$ 1.03	$Zn$ 2.0	$KCl$ 1	4.20	4.68	4.83
(B)	$Tl$ 0.975	$Ni$ 2.0	$KNO_3$ 1	3.71		3.69
$O_2$ irreversible	$Cd$ 1.03	$Ni$ 2.0	$NH_3-NH_4Cl$ 1	5.00		5.09
(C)	$Cd$ 1.03	$Zn$ 2.0	$NH_3-NH_4Cl$ 1	(1)4.57 <sup>a</sup> (2)5.00 <sup>b</sup>	(1)5.09	5.11
$R_2$ reoxidized						

<sup>a</sup> First wave

<sup>b</sup> Sum of first and second waves (capillary A).

$Zn^{2+}$  and  $O_s$  is  $NH_3-NH_4Cl$  buffer solution. It is well known from amalgam polarography that  $Zn^{2+}$  is reduced at about  $-1.3$  V vs. a S.C.E., while its amalgam is re-oxidized at  $-1.1$  V. Figure 6 shows the waves obtained for this system. A small wave appears clearly at the re-oxidation potential of Zn amalgam, the height of which is about 10% of that of the Cd wave. This small second wave is a characteristic feature of the current-scan polarogram at the D.M.E. (the dotted line is the conventional polarogram).

#### The effect of small amounts of the substance reduced at more negative potentials

To test the effects of small amounts of  $O_2$  on the limiting current of  $O_1$  shown in Fig. 3, the value  $i_l/(i_l)_{max}$  was measured as a function of  $K'$ , which is the ratio of the wave

height of  $O_1$  and  $O_2$  in conventional polarography. This ratio can be regarded as being equal to  $K$  when the variation of drop-time with electrode potential is neglected.

As is shown in Figs. 7 and 8, the value measured experimentally is in fairly good agreement with the theoretical value (the solid line shows the theoretical results).

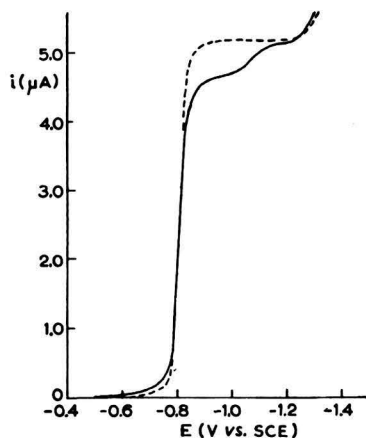


Fig. 6. Current-potential curves of 1.03 mM  $\text{Cd}^{2+}$  in 2.0 mM  $\text{Zn}^{2+}$ , 1 M  $\text{NH}_3\text{-NH}_4\text{Cl}$  solution. Solid line, current scan method; dotted line, conventional method (maximum current) (capillary A).

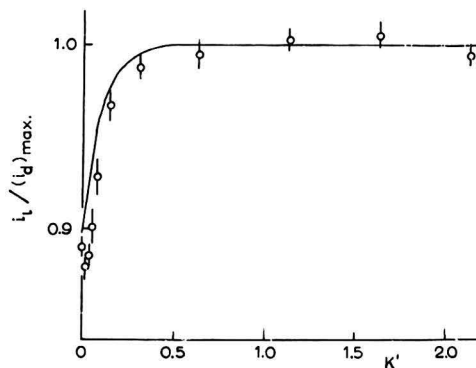


Fig. 7. Relation between the limiting current of  $O_1$  and the concentration of  $O_2$ . (1) When the reduction of  $O_2$  is reversible, while that of  $O_1$  is totally irreversible:  $O_1$ , 0.500 mM  $\text{Cu}^{2+}$ ;  $O_2$ ,  $\text{IO}_3^-$  (totally irreversible);  $O_2$ , 4 mM  $\text{Zn}^{2+}$  (reversible) in 0.1 N NaOAc; HOAc (pH = 4.6).  $K'$  is the ratio of the wave heights of  $\text{Cu}^{2+}$  and  $\text{IO}_3^-$  in the conventional method. The solid line shows the theoretical value.

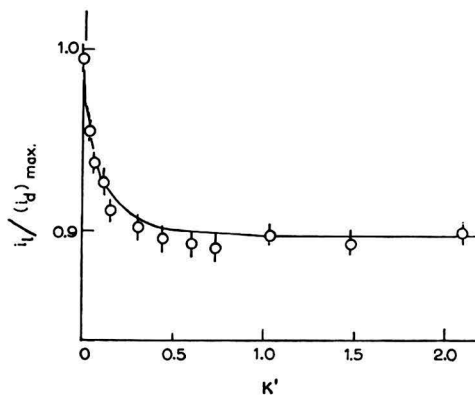


Fig. 8. Relation between the limiting current of  $O_1$  and the concentration of  $O_2$ . (2) When the reduction of  $O_2$  is totally irreversible, while that of  $O_1$  is reversible:  $O_1$ , 0.500 mM  $\text{Tl}^+$ ;  $O_2$ ,  $\text{Cd}^{2+}$ ;  $O_2$ , 4.0 mM  $\text{Ni}^{2+}$  in 1 M  $\text{NH}_3\text{-NH}_4\text{Cl}$ .  $K'$  is the ratio of wave heights of  $\text{Tl}^+$  and  $\text{Cd}^{2+}$  in the conventional method. The solid line shows the theoretical value.

#### The application to quantitative analysis of two-component systems

From the above results, the current-scanning method can be applied for quantitative determination of two components. By using the values given in Tables I and II, the

relation between the value of  $K$  and the ratio of the wave heights of  $O_1$  and  $O_2$  can be calculated and shown graphically. In order to determine the concentrations of  $O_1$  and  $O_2$  by this method, the ratio of their wave heights is measured initially. From this ratio, and the theoretical relations obtained above, we can find the value of  $K$ , and the limiting currents of  $O_1$  and  $O_2$  can be corrected for the case in which each of them is present separately in the solution of  $O_s$ . If we have calibration curves for  $O_1$  and  $O_2$  when present separately in the solution of  $O_s$  (supporting electrolyte), we know the concentra-

TABLE IV

DETERMINATION OF TWO COMPONENTS:  $O_2$  AND  $O_s$  ARE REVERSIBLY REDUCED

Electrolytic solution: 0.1  $M$  KCl; 4  $mM$  Zn ( $O_s$ ); 0.02% PAA and Pb ( $O_1$ ), Cd ( $O_2$ ) (capillary B).  
The limiting current was corrected for the residual current<sup>4</sup>.

$C_{Pb}$ ( $mM$ )	$C_{Cd}$ ( $mM$ )	$i_{Pb}$ ( $\mu A$ )	$i_{Pb}/C_{Pb}$	$i_{Cd}$ ( $\mu A$ )
0	0.125	0	—	0.671
0.152	0.125	0.756	6.05	0.672
0.375	0.125	2.301	6.15	0.656
0.625	0.125	3.840	6.15	0.656
0.875	0.125	5.33	6.12	0.672
1.375	0.125	8.47	6.16	0.664

TABLE V

DETERMINATION OF TWO COMPONENTS: THE REDUCTION OF  $O_s$  IS IRREVERSIBLE, AND THAT OF  $O_2$  IS REVERSIBLE

Electrolytic solution: 0.5  $N$  HClO<sub>4</sub> ( $O_s$ ); 0.02% PAA; 0.125  $mM$  Cd ( $O_2$ ) and Pb ( $O_1$ ) (capillary B)

$C_{Pb}$ ( $mM$ )	$i_{Pb}$ ( $\mu A$ )	$i_{Cd}$ ( $\mu A$ )	$i_{Cd}/i_{stat}$	$K$	$(i_{Cd})_{corr.}$	$(i_{Pb})_{corr.}/C_{Pb}$
0	0	0.711	1.000	—	(0.711)	—
0.125	0.785	0.791	0.491	—	0.705	6.94
0.375	2.300	0.919	0.285	0.271	0.686	6.77
0.875	5.66	1.137	0.168	0.114	0.692	6.95
1.375	8.82	1.290	0.127	0.074	0.699	6.88

tions of  $O_1$  and  $O_2$  immediately. Some examples are shown in Tables IV and V. Table IV shows the cases when the reductions of  $O_2$  and  $O_s$  are both reversible. The concentrations of  $O_1$  and  $O_2$  can be determined only by measuring their wave heights. We need no correction for the limiting currents, except for the residual currents. Table V, on the other hand, shows the cases in which the reduction of  $O_s$  is totally irreversible, and that of  $O_2$  is reversible. As is apparent from Table V, the corrected limiting currents are proportional to their concentrations, which shows the applicability of this method for analytical purposes.

## ACKNOWLEDGEMENTS

The authors wish to express their sincere thanks to Emeritus Prof. MASAYOSHI ISHIBASHI for his helpful encouragement throughout this work.

## SUMMARY

In current-scanning polarography at the D.M.E., the limiting current  $i_l$  of a reducible substance  $O_1$  is affected by the electrode reaction of a substance reduced at more negative potentials. The value of the limiting current was calculated for the cases in which (1) the concentration of the second constituent  $O_s$  is much larger than that of  $O_1$ , and (2) the solution contains a substance  $O_2$ , which is reducible at a potential between the reduction potentials of  $O_1$  and  $O_s$ . The results were in fairly good agreement with the values obtained experimentally. It is suggested that the current-scanning method is applicable for analytical purposes.

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## THE SEPARATION OF INORGANIC IONS BY ELECTROPHORESIS ON PAPER IMPREGNATED WITH ION EXCHANGERS

G. ALBERTI, A. CONTE, G. GRASSINI AND M. LEDERER

*Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N., and Laboratorio di Cromatografia del C.N.R., Istituto di Chimica Generale ed Inorganica, Rome (Italy)*

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The advantages of ion exchange papers (modified cellulose, resin impregnated or impregnated with inorganic exchangers) in chromatographic work have been shown in numerous papers<sup>1-7</sup>.

Work on electrophoresis in ion exchange materials has so far been limited to columns filled with resins<sup>8</sup> and to some preliminary work on resin papers, with amino acids and alkaline earths<sup>9</sup>. Furthermore, some electrophoretic experiments with home-made Dowex-50 papers yielded indifferent results, with distorted zones (M. LEDERER, unpublished results).

It was thus considered of interest to study factors influencing the movement of inorganic substances when subjected to an electric field on ion exchange papers as *a priori* improved separations would be expected.

## EXPERIMENTAL

Amberlite SA 2 paper and filter paper impregnated with zirconium phosphate (for its preparation see<sup>6</sup>) were employed in this work. Paper electrophoresis was carried out as described by LEDERER AND WARD<sup>10</sup> with glass plates 2.5 cm × 45 cm and a voltage of 4.7 V/cm.

$R_f$  values were measured after development at 50°, this temperature corresponding approximately to that of the paper strips during electrophoresis.

## RESULTS AND DISCUSSION

If a certain ion has a mobility  $U$  on ordinary paper, its mobility  $U_i$  on ion exchange paper is usually less, due to the interaction between the ion and the exchanger. The difference between the two mobilities should increase with the affinity of the ion for the ion exchanger, as we could confirm with the alkali group cations, whose affinity increases from lithium to caesium (Table 1). Since the  $R_f$  values on ion exchange paper are related to the affinity of the ion for the exchanger, the electrophoretic mobility on ion exchange papers can be expressed in terms of the chromatographic  $R_f$  value. The simplest approach is, that we look at electrophoresis on ion exchange papers as a form of chromatography, in which the "solvent" moves the distance an ion moves on ordinary paper. The  $R_f$  value then corresponds to the ratio of the mobil-

ity on ion exchange paper to that on ordinary paper. This can also be expressed mathematically as:

$$R_f = K \frac{U_i}{U} \quad (1)$$

where  $K$  is a constant accounting for the differences of experimental conditions (paper thickness etc.) between ordinary and ion exchange papers. For example, Whatman No. 1 paper when loaded with ion exchange resins will hold a larger amount of electrolyte, and thus change the current passed, under otherwise identical conditions of electrophoresis. The ionic mobilities in eqn. (1) are calculated from experimental results by correcting for electro-osmotic flow.

TABLE I

PAPER ELECTROPHORESIS OF THE ALKALIS ON WHATMAN NO. 1 PAPER AND ON WHATMAN NO. 1 PAPER IMPREGNATED WITH ZIRCONIUM PHOSPHATE

Electrolyte, 0.5 N HCl; electric field, 4.7 V/cm; time, one h.

Ion	Distance moved (in cm) on Whatman No. 1 paper	Distance moved (in cm) on Whatman No. 1 paper impregnated with zirconium phosphate
Li(I)	5	4
Na(I)	6	4.5
K(I)	8	6
Rb(I)	7.5	2.5
Cs(I)	7.5	0

On cellulose paper, mobilities were corrected by adding or subtracting the distance moved by hydrogen peroxide under the conditions of the electrophoretic experiment. With the electrolytes used here (strong acids or salts), adsorption on the cellulose can be considered negligible. Thus, the mobility on cellulose paper is  $U = U_{\text{exp}} \pm u_e$ , where  $u_e$  is the electro-osmotic flow.

On ion exchange paper, the correction for electro-osmotic flow must be multiplied by the chromatographic  $R_f$  value of the ion examined, because when the liquid is displaced a certain distance, the ion moves a smaller distance only, depending on its affinity for the resin. The corrected mobility on ion exchange paper is then  $U_i = U_{i \text{ exp}} \pm u_{ei} R_f$ , where  $u_{ei}$  is the movement of hydrogen peroxide on the ion exchange paper under the conditions of the electrophoretic experiment.

Substituting these expressions in eqn. (1) we obtain:

$$R_f = K \frac{U_{i \text{ exp}} \pm u_{ei} R_f}{U_{\text{exp}} \pm u_e} \quad (2)$$

The factor  $K$ , which depends mainly on the type of paper employed, can be determined experimentally by a number of mobility determinations on ordinary and resin loaded paper. If  $K$  is known, the mobility  $U_i$  of a given ion can be predicted for an ion exchange paper, if its mobility on ordinary paper and its  $R_f$  value on the resin paper are known. Table II shows the experimental and calculated mobilities on paper impreg-

nated with zirconium phosphate (ZP paper) and Table III shows mobilities for filter papers loaded with a strong sulphonic resin, (Amberlite SA 2 paper). The agreement seems to be satisfactory, considering the accuracy of the measurements involved (which depends on the accuracy of the distance measured, the variation of temperature, etc.).

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL MOBILITIES OF SOME INORGANIC IONS ON WHATMAN NO. 1 PAPER IMPREGNATED WITH ZIRCONIUM PHOSPHATE

Electrolyte, 0.5 N HCl; electric field, 4.7 V/cm; time, one h.

Ion	Chromatographic $R_f$ value at 50° on ZP paper with 0.5 N HCl as eluant	Distance moved (in cm) on Whatman No. 1 paper, corrected for electro-osmotic flow	Distance moved (in cm) calculated using eqn. (2) and taking $K = 1.215$	Distance moved (in cm) on ZP paper, found experimentally
Li(I)	0.9	4.9	4.0	4
Na(I)	0.8	5.9	4.2	4.5
Rb(I)	0.5	7.4	3.2	2.5
Sr(II)	1	4.4	4.0	4.5
Ni(II)	0.8	4.6	3.4	3.6
Co(II)	0.9	5	4.0	3.5
Zn(II)	1	3.2	3.0	3
Cu(II)	0.9	4.3	3.6	3.8
U(VI)	0.1	2.4	0.2	0.3
Fe(III)	0	2.5	0	0
Al(III)	0.2	3.6	0.8	0.8
La(III)	0.8	4.1	3.0	3
Th(IV)	0	3.9	0	0

TABLE III

COMPARISON OF THE CALCULATED AND EXPERIMENTAL MOBILITIES OF SOME INORGANIC IONS ON AMBERLITE SA 2 PAPER

Electrolyte, 0.1 N HCl-0.9 N KCl; electric field, 4.7 V/cm; time, one h.

Ion	Chromatographic $R_f$ value at 60° on Amberlite SA 2 paper (potassium form) with 0.1 N HCl-0.9 N KCl as eluant	Distance moved (in cm) on Whatman No. 3 paper, corrected for electro-osmotic flow	Distance calculated (in cm) using eqn. (3), and taking $K = 0.712$	Distance moved (in cm) on Amberlite SA 2 paper, found experimentally
Cs(I)	0.61	7.8	6.7	7
Co(II)	0.37	3.8	2	2.1
Cu(II)	0.52	3.4	2.5	2.3
UO <sub>2</sub> (II)	0.1	2.5	0.4	0.4
Al(III)	0.1	4.5	0.6	0.6

Equation (2) expresses  $U_i$  in terms of  $R_f$  and  $U$ . The mobility  $U_i$  may, however, also be expressed in terms of the charge on the ion and the concentration of the electrolyte used, similar to the approach used for ion exchange chromatography by LEDERER AND KERTES<sup>2</sup> who proposed the eqn.

$$\alpha pH = \log \left( \frac{1}{R_f} - 1 \right) + \text{const.} \quad (3)$$

for strong resins developed with strong acids ( $x$  is the charge of the ion). If this eqn. (3) is combined with eqn. (1) we obtain:

$$x\text{pH} = \log \left( \frac{U}{U_i} - 1 \right) + \text{const.} \quad (4)$$

Equation (4) can only be applied to papers loaded with a strong ion exchanger. As we have shown previously<sup>6</sup>, eqn. (3) is not valid for weak ion exchangers such as zirconium phosphate.

If, however, a salt is used as electrolyte (pH = neutral), an analogous relationship may be obtained:

$$-\frac{x}{n} \log [A M e^{+n}] = \log \frac{(U - U_i)}{U_i} + \text{const.} \quad (5)$$

where ( $M e^{+n}$ ) is the concentration of the cation of the electrolyte used, and  $A$  is a constant which depends on the affinity of the cation  $M e^{+n}$  for the exchanger. From eqn. (5) it can be seen that  $U_i$  approaches  $U$  as the concentration of  $M e^{+n}$  increases. Also, as the affinity of  $M e^{+n}$  for the exchanger increases (and thus the value of  $A$ ), the mobility  $U_i$  will increase. Now, the affinity of an ion for an exchanger depends on the radius of the hydrated ion and decreases for alkalis in the following sequence: Cs > Rb > K > Na > Li.

Thus the mobility  $U_i$  is greater when KCl is employed as electrolyte than when NaCl is used. When acids are used as electrolytes, the great affinity of weak exchangers and lesser affinity of strong exchangers for the  $H^+$  ion must be taken into account. Hence, with a weak exchanger such as zirconium phosphate, the mobility in 0.5  $N$  HCl is greater than with 0.5  $N$  KCl. The opposite may be observed with a paper loaded with a strong cationic resin, such as Amberlite SA 2 paper. Hence, if it is desired to increase the mobility  $U_i$  on strong resin paper without increasing the acidity (which would increase the current passed) the potassium form of the paper with KCl as electrolyte may be employed. The substitution of potassium ions for hydrogen ions also permits operation in electrolyte concentrations higher than those possible with acids, without an undue increase in the current intensity.

For example, the mobilities of Co(II), Cu(II), Ni(II) and Cs(I) are 2 to 3 times as great in  $N$  KCl as in 0.5  $N$  HCl, the current passed in both cases being about equal.

#### SEPARATION OF INORGANIC IONS

The analytical possibilities of separations of the ions  $A^{+n}$  and  $B^{+n}$  on papers loaded with exchangers can be considered in terms of the mobilities on ordinary cellulose paper and  $R_f$  values on resin paper as follows.

##### Case 1

$$R_{fA^{+n}} = R_{fB^{+n}}, \text{ mobility } A^{+n} = \text{mobility } B^{+n}$$

In this case, a separation is impossible by ion exchange chromatography, by electrophoresis on ordinary paper, or by electrophoresis on ion exchange paper. As shown in Table II, Co(II) and Ni(II) having the same mobilities, and  $R_f$  values on ZP paper, can not be separated by electrophoresis on paper impregnated with zirconium phosphate.

## Case 2

$$R_{f_{A^{+n}}} \neq R_{f_{B^{+n}}}, \text{ mobility } A^{+n} = \text{ mobility } B^{+n}$$

A separation is possible by ion exchange chromatography, but not by electrophoresis on cellulose paper. It is also possible by electrophoresis on ion exchange paper. Here, the separation is due only to the differences in ion exchange affinities of the two ions.

TABLE IV

ELECTROPHORETIC MOBILITIES ON CELLULOSE PAPER AND  $R_f$  VALUES ON ZP PAPER OF THE RARE EARTHS

Electrophoresis: Whatman No. 1 paper; electrolyte, 0.5 N HClO<sub>4</sub>; electric field, 4.7 V/cm; time, two h. Chromatography: Whatman No. 1 paper impregnated with zirconium phosphate; temperature, 50°; eluant, 0.5 N HClO<sub>4</sub>.

Ion	Distance moved (in cm)	$R_f$ value
La(III)	13.3	0.56
Ce(III)	13.3	0.49
Pr(III)	13.3	0.45
Nd(III)	13.8	0.40
Sm(III)	13	0.26
Eu(III)	13.8	0.24
Gd(III)	13	0.21
Tb(III)	13.1	0.23
Dy(III)	12.6	0.25
Ho(III)	12.4	0.19
Er(III)	12.4	0.18
Tu(III)	12.4	0.17
Yb(III)	11.7	0.15
Lu(III)	11.2	—

Some examples are shown in Table IV, where some lanthanides are separated employing 0.5 N HClO<sub>4</sub> as eluant in chromatography and as electrolyte. While separations on cellulose papers are not possible, they may be effected amongst some of the rare earths by electrophoresis on paper loaded with ZP, as well as by chromatography on ZP paper. (See Fig. 1.)

## Case 3

$$R_{f_{A^{+n}}} = R_{f_{B^{+n}}}, \text{ mobility } A^{+n} \neq \text{ mobility } B^{+n}$$

A separation is not possible by chromatography on ion exchange paper, but it is possible by electrophoresis on cellulose paper, and also by electrophoresis on ion exchange paper. In the last case, the separation is solely due to the difference in the ionic mobilities. Figure 2 shows an example of the separation of Cd-Ni on Whatman No. 3 paper and Amberlite SA 2 paper.

## Case 4

$$R_{f_{A^{+n}}} \neq R_{f_{B^{+n}}}, \text{ mobility } A^{+n} \neq \text{ mobility } B^{+n}$$

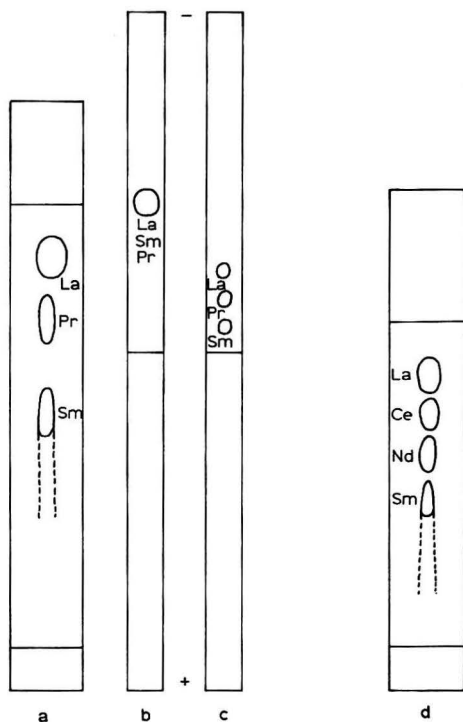


Fig. 1. (a), Chromatogram of La, Pr and Sm on ZP paper with 0.5 *N* HClO<sub>4</sub> as eluant. (b), Electrophoresis of a mixture of La-Pr-Sm on Whatman No. 1 paper. (c), as (b) using ZP paper. (d), Chromatogram of a mixture of La-Ce-Nd-Sm on ZP paper with 0.5 *N* HClO<sub>4</sub> as eluant.

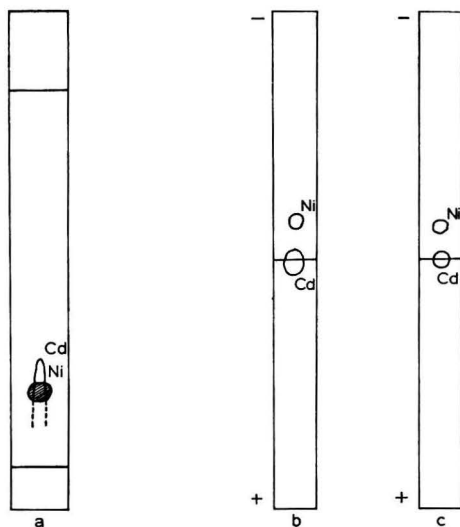


Fig. 2. (a), Chromatogram of Cd(II) and Ni(II) on Amberlite SA 2 paper with 0.1 *N* HCl-0.9 *N* KCl as eluant. (b), Electrophoresis of a mixture of Cd(II) and Ni(II) on Whatman No. 3 paper with 0.1 *N* HCl-0.9 *N* KCl as electrolyte. (c), as (b) using Amberlite SA 2 paper instead of Whatman No. 3.

Separations are possible by chromatography and by electrophoresis on cellulose paper, as well as on resin loaded paper. If  $R_{fA^{+n}} > R_{fB^{+n}}$ , and mobility  $A^{+n} >$  mobility  $B^{+n}$ , the effects of mobility and exchange affinity supplement one another, producing a better separation than is possible by using each process separately. If, however,  $R_{fA^{+n}} > R_{fB^{+n}}$ , but mobility  $A^{+n} <$  mobility  $B^{+n}$ , the two separating

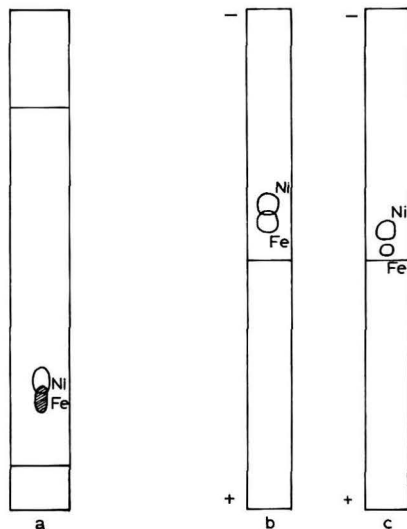


Fig. 3. (a), Chromatogram of a mixture of Fe(III)-Ni(II) on Amberlite SA 2 paper with 0.1 *N* HCl-0.9 *N* KCl as eluant. (b), Electrophoresis of a mixture of Fe(III) and Ni(II) on Whatman No. 3 paper. (c), as (b) using Amberlite SA 2 paper instead of Whatman No. 3.

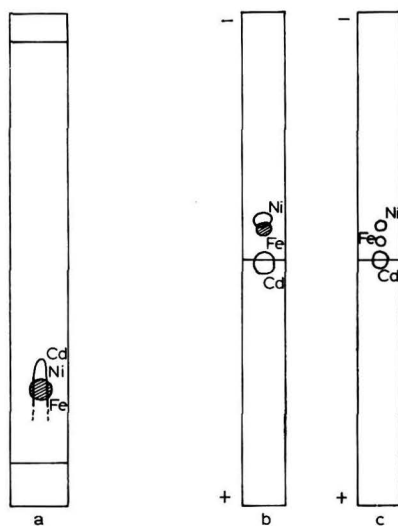


Fig. 4. (a), Chromatogram of a mixture of Fe(III)-Ni(II)-Cd(II) on Amberlite SA 2 paper with 0.1 *N* HCl-0.9 *N* KCl as eluant. (b), Electrophoresis of a mixture of Fe(III)-Ni(II)-Cd(II) on Whatman No. 3 paper with 0.1 *N* HCl-0.9 *N* KCl as electrolyte. (c), as (b) using Amberlite SA 2 paper instead of Whatman No. 3.

effects interfere with each other and a poorer separation is obtained than by using each process separately. An example of an improved separation is shown in Fig. 3, which shows the separation of Fe(III) and Ni(II) on Amberlite SA 2 paper.

Another case where electrophoresis on ion exchange paper may be applied is the simultaneous separation of three ions  $A^{+n}$ ,  $B^{+n}$ , and  $C^{+n}$ . If, for example,  $R_{fA^{+n}} = R_{fB^{+n}} \neq R_{fC^{+n}}$  and mobility  $A^{+n} \neq$  mobility  $B^{+n} =$  mobility  $C^{+n}$ , a separation would be impossible by either ion exchange chromatography or cellulose paper electrophoresis, but there would be a separation by electrophoresis on ion exchange paper. Such a case is shown in Fig. 4, *i.e.* the separation Fe(III)–Ni(II)–Cd(II).

#### CONCLUSIONS

Electrophoresis on ion exchange paper may be considered as a form of ion exchange chromatography, in which each ion is developed for a distance proportional to its electrophoretic mobility on cellulose paper.

It was shown that various cases exist where electrophoresis on ion exchange papers presents advantages over either electrophoresis on cellulose paper, or chromatography on ion exchange paper.

The method seems to have possible applications in numerous analytical problems concerning the separation of complex mixtures of inorganic ions.

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POTENTIOMETRIC ACID-BASE TITRATIONS IN MOLTEN SALTS.  
THE SYSTEM  $\text{Cr}_2\text{O}_7^{2-}$ - $\text{CrO}_4^{2-}$ - $\text{O}^{2-}$

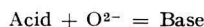
A. M. SHAMS EL DIN AND A. A. A. GERGES

*Laboratory of Electrochemistry and Corrosion, National Research Centre, Dokki, Cairo (U.A.R.)*

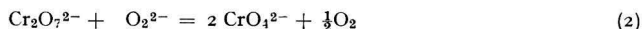
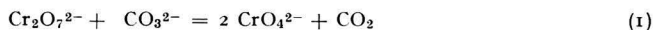
(Received January 18th, 1962)

Recently one of the present authors (A.M.S.D.) reported the first known example of potentiometric acid-base titrations in melts<sup>1</sup>. The case studied was the titration of the acids  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CrO}_3$  with solid KOH in molten  $\text{KNO}_3$ . The titrant was added to the melt in the form of small weighed pellets and the potential of an oxygen (Pt) electrode was measured against a suitable reference electrode. At the equivalence point, a drop in the potential of the indicator electrode of *ca.* 700 mV was measured.

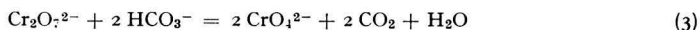
Because water is a product of these reactions, it was feared that its presence in traces in the melt might vitiate the measured potentials. The present study was, therefore, undertaken to investigate this particular point. Two new bases, *viz.*,  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{O}_2$  were used to titrate the acid  $\text{K}_2\text{Cr}_2\text{O}_7$ . Their reactions with the acid do not lead to the formation of water, and hence the titration was considered to be conducted under perfectly anhydrous conditions. A third base,  $\text{NaHCO}_3$ , was similarly investigated. The general neutralisation reaction is represented by:



Specifically mentioned, the reactions are:



and



With all the three bases investigated, the points of maximum inflexion of the potentiometric titration curves coincided in practice with the theoretical quantities of the bases necessary to neutralise the acid. The titration curves were not at all, or only slightly, affected by the presence of traces of water in the melt.

#### EXPERIMENTAL

Titration were carried out in tall unlippped Pyrex-glass beakers, completely surrounded by an electrically heated furnace. The temperature of the melt was measured by means of a platinum-platinum-10% rhodium thermocouple enclosed in a tight-fitting glass mantle dipping directly into the melt. The oxygen indicator electrode was a platinised  $1 \times 1$  cm platinum foil. By means of a glass tube, whose tip was brought

into close proximity with the indicator electrode, pure dry oxygen was made to bubble into the melt at a rate of 2–3 bubbles per second.

The reference electrode was a 99.9+ % silver wire dipping into a silver nitrate–potassium nitrate melt (2.04%  $\text{AgNO}_3$  w/w). The electrode was separated from the main melt by means of a small G 4 sintered glass disc.

$\text{KNO}_3$  acted as a diluent in the titration. The analytically pure sample was pre-melted and the last traces of water were expelled by bubbling pure dry oxygen for a period of 1 h. The solidified salt was then crushed in a mortar and kept in a desiccator until required.

50.00 g of the nitrate, together with the weighed quantity of the dichromate were melted over a period of 2 h. The electrodes were then slowly lowered into position, and oxygen was bubbled into the melt. This resulted in the direct establishment of a steady potential. The titration was carried out by adding weighed quantities of the base. Changes in potential were observed. These depended on the type of base used, and on the progress of the neutralisation process. The peroxide required relatively longer periods for the potential to reach a constant value, especially near the end-point. The measured potentials were reproducible to better than  $\pm 25$  mV.

#### RESULTS AND DISCUSSION

In Fig. 1 potentiometric titration curves for different concentrations of the acid  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{Na}_2\text{CO}_3$  base are shown. Figures 2 and 3 are the same, using the bases

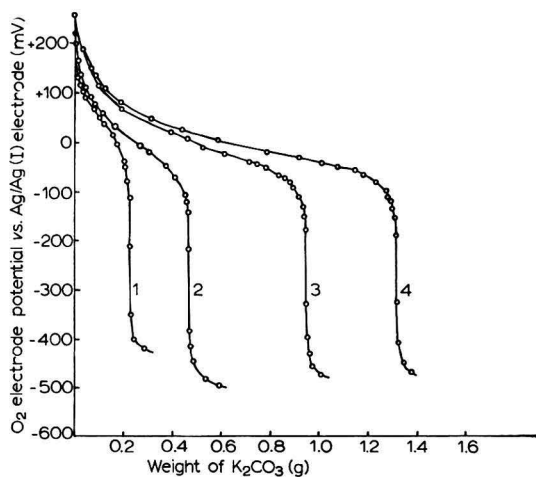


Fig. 1. Potentiometric titration of  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{K}_2\text{CO}_3$  at  $350^\circ$ . (1), 0.500 g; (2), 1.000 g; (3), 2.000 g and (4), 2.800 g  $\text{K}_2\text{Cr}_2\text{O}_7$  per 50.00 g  $\text{KNO}_3$ .

$\text{Na}_2\text{O}_2$  and  $\text{NaHCO}_3$ . In all these titrations 50.00 g of  $\text{KNO}_3$  were used as a diluent and the temperature of the melt was kept constant at  $350^\circ$ . As can be seen from the Figs., the variation of the potential of the oxygen electrode with the quantity of base followed typical potentiometric titration curves. During the titration, the original orange red colour of the melt changed to the light yellow colour characteristic of

chromates. At the equivalence point a sharp drop in the potential of the indicator electrode occurred, whose magnitude depended on the particular base used; it was greatest for  $\text{Na}_2\text{O}_2$ . The carbonate and the bicarbonate gave comparable potential drops. With the carbonate acting as the base, a deposit was observed at and after the

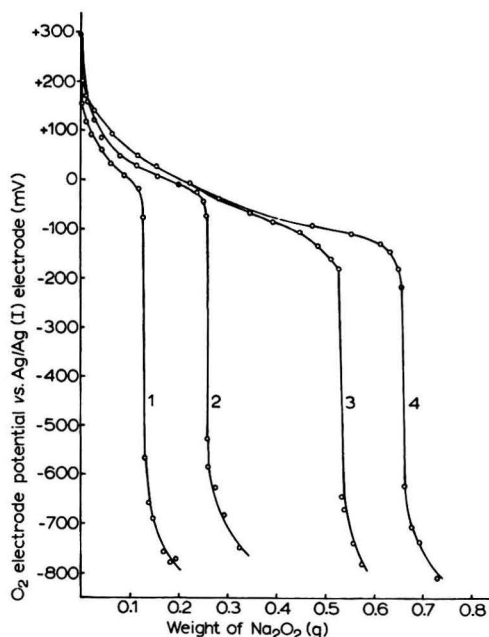


Fig. 2. Potentiometric titration of  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{Na}_2\text{O}_2$  at  $35^\circ$ . (1), 0.500 g; (2), 1.000 g; (3), 2.000 g and (4), 2.500 g  $\text{K}_2\text{Cr}_2\text{O}_7$  per 50.00 g  $\text{KNO}_3$ .

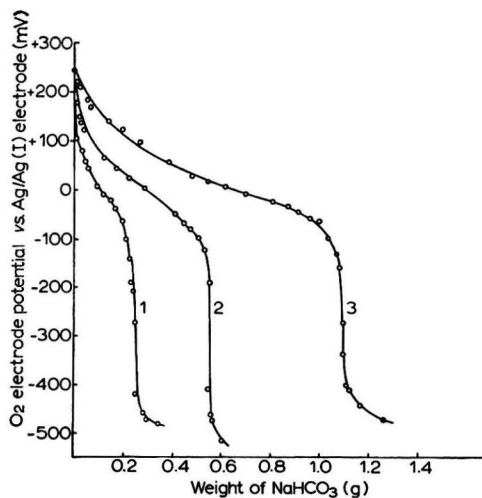


Fig. 3. Potentiometric titration of  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{NaHCO}_3$  at  $35^\circ$ . (1), 0.500 g; (2), 1.000 g and (3), 2.000 g  $\text{K}_2\text{Cr}_2\text{O}_7$  per 50.00 g  $\text{KNO}_3$ .

equivalence point. This deposit did not persist in aqueous solutions of the solidified melts and is apparently the carbonate itself, which is insoluble in the melt at this low temperature.

As is seen from Figs. 1-3, the potential of the oxygen electrode is - within experimental error-independent of whether the melt is completely dry ( $\text{Na}_2\text{O}_2$  and  $\text{K}_2\text{CO}_3$ ) or contaminated with traces of water ( $\text{NaHCO}_3$ ). The presence of water as an impurity in the melt under investigation does not seem, therefore, to affect the results.

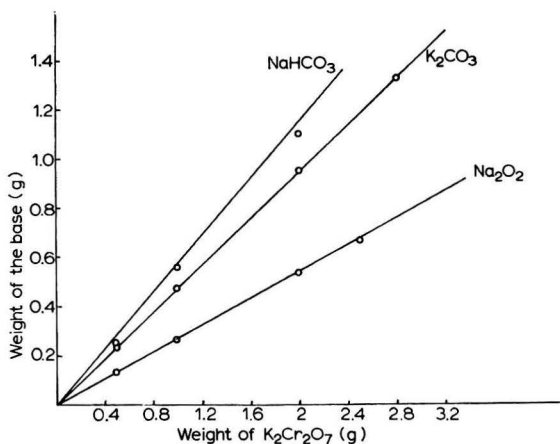


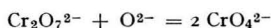
Fig. 4. Relationship between the quantities of the bases and the concentration of the dichromate. Points show experimental values and the lines are calculated theoretically.

In Fig. 4 the weights of the three bases consumed before the inflexion points of the titration curves are plotted as a function of the corresponding weights of dichromate in the melt. The circles are the experimental points obtained from differential titration curves, while the solid lines are drawn according to theory. The agreement between the two sets of figures is quite clear.

Theoretical analysis of the titration curves was previously given<sup>1</sup>. The potential of the oxygen electrode during the course of the titration could be given in the form:

$$E = E^\circ + \frac{RT}{2F} \log K - \frac{RT}{2F} \log \frac{[\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} \quad (4)$$

where  $E^\circ$  is the standard  $\text{O}_2/\text{O}^{2-}$  potential relative to our reference electrode and  $K$  is the equilibrium constant of the reaction:



Expressing the potential in terms of weights rather than molar concentrations, eqn. (4) becomes:

$$E = E^\circ + \frac{RT}{2F} \log K - \frac{RT}{2F} \log \frac{w^2}{(w_e - w)} = E^{\prime\prime} - \frac{RT}{2F} \log \frac{w^2}{(w_e - w)} \quad (5)$$

where  $w$  is the weight of the base added,  $w_e$  is the total weight of base needed to neutralise the acid completely, and  $\hat{E}^\circ$  incorporates a proportionality factor converting the weights to corresponding moles. The plot of the potential  $E$  against the function  $\log w^2/(w_e-w)$  should produce a straight line, whose slope equals the value of  $3.303 RT/2F$  at  $350^\circ$  (61.6 mV). All the three bases gave the expected result. Figure 5 gives an example of the analysis of the titration curves obtained with the carbonate acting as the base.

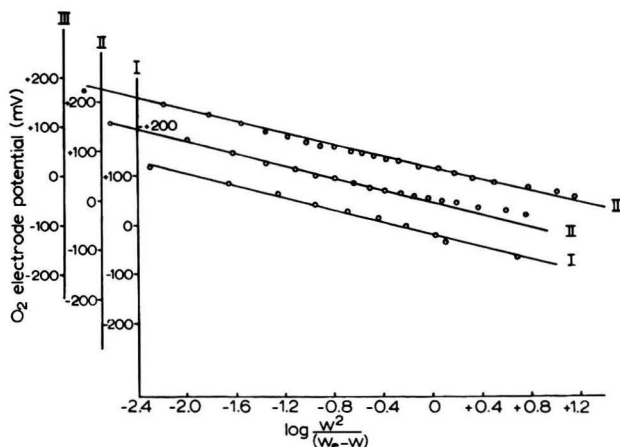


Fig. 5. Theoretical analysis of the titration curves using carbonate as the base. (1), 0.500 g; (2), 1.000 g and (3), 2.000 g  $K_2Cr_2O_7$  per 50 g  $KNO_3$ .

The points in Fig. 5 were taken by interpolation of the points from Fig. 1, while the solid lines were drawn with a theoretical slope of  $2.303 RT/2F$ . The experimental points are seen to fall satisfactorily on the theoretical lines, suggesting that the above analysis is correct. Average values for  $\hat{E}^\circ$  are successively  $-5$  mV,  $-40$  mV, and  $-15$  mV for the carbonate, peroxide, and bicarbonate respectively, using a  $Ag/Ag(I)$  reference electrode. Within the limits of experimental error, the  $\hat{E}^\circ$  term is constant for the three titrants. This again supports the conclusion that contamination of the melt under investigation by traces of water does not affect the results of the potentiometric titrations.

#### SUMMARY

The acid  $K_2Cr_2O_7$  was titrated potentiometrically against the three bases  $K_2CO_3$ ,  $Na_2O_2$ , and  $NaHCO_3$  in molten  $KNO_3$  at  $350^\circ$ . An oxygen electrode was used as an indicator electrode, while a  $Ag/Ag(I)$  electrode acted as a suitable reference electrode. At the equivalence point, a sharp drop in the potential of the indicator electrode was measured, whose magnitude depended on the base used. The points of maximum inflexion in the titration curves were identical with the theoretical quantities of the bases necessary for neutralisation of the acid. Contamination of the melt with traces of water did not affect the measured potentials.

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## Short Communications

### On the definition of pH

In our previous note on the definition of pH<sup>1</sup> we suggested that, at low ionic strengths of solutions containing known molalities of the anion  $i$  and the cation  $j$ , pH be defined as:

$$\text{pH} = -\log Q_{ij} \quad (1)$$

with, for univalent ions:

$$Q_{ij} = (N_i P_j m_j / m_i)^{\frac{1}{2}} \quad (2)$$

where

$$N_i = a_{\text{H}^+} a_i$$

and

$$P_j = a_{\text{H}^+} / a_j \quad (3)$$

the  $m$ 's being molalities and the  $a$ 's activities.

We easily see that:

$$\text{pH} = -\log(a_{\text{H}^+} \gamma_i^{\frac{1}{2}} / \gamma_j^{\frac{1}{2}}) \quad (4)$$

the  $\gamma$ 's being activity coefficients. The quantities  $N_i$  and  $P_j$  are separately measurable in cells without liquid junctions, the electrodes being in one case Pt, H<sub>2</sub> and an insoluble salt of the anion  $i$  with the corresponding metal, in the other case Pt, H<sub>2</sub> and the metal corresponding to  $j$  or an amalgam of this metal. With  $i = \text{Cl}^-$  and  $j = \text{K}^+$ , for instance, we have:

$$\text{pH} = -\log(a_{\text{H}^+} \gamma_{\text{Cl}^-}^{\frac{1}{2}} / \gamma_{\text{K}^+}^{\frac{1}{2}}) \quad (5)$$

If MACINNES' assumption concerning the equality of  $\gamma_{\text{Cl}^-}$  and  $\gamma_{\text{K}^+}$ <sup>2</sup> were to be verified<sup>2</sup>, we would indeed have:

$$\text{pH} = \text{p}a_{\text{H}^+} \quad (6)$$

If the determination of pH is repeated with other  $ij$  pairs (whether these various ions are originally present in the solution under study or are added to it, the measurements being in this latter case extrapolated to zero molality of the added electrolyte) it may be expected that, for sufficiently low ionic strengths, the various  $Q_{ij}$  values will all be equal to one another. A true single ion activity would thus have been obtained experimentally. This possibility suggests what we regard as a very interesting research topic.

At the higher ionic strengths the various  $Q_{ij}$  values will tend to differ from one another on account of the specific interaction effects. For such cases we have suggested that a geometrical average,

$$\text{pH} = -\log [II (Q_{ij})]^{1/k} \quad (7)$$

$k$  being the number of anion species and  $l$  the number of cation species considered, could be regarded as a close approximation to the true  $\text{p}a_{\text{H}^+}$ . It may indeed be ex-

pected that the various  $\gamma_i^{1/3}/\gamma_j^{1/3}$  ratios (see formula (4)), being in some cases greater than one and in other cases smaller than one, will give a product in which these departures from one are somewhat compensated. Moreover, the  $k$ th root of this product will be closer to one than the product itself. The experimental exploration of these possibilities would be of the greatest interest.

In practice, pH determinations are often carried out in order to obtain information, at least in the form of an approximation, on the actual concentration or molality  $m_{\text{H}^+}$  of the hydrogen ion. In the case of low ionic strengths we could use formula (5) and transform it into:

$$\text{pH} = -\log(m_{\text{H}^+}\gamma_{\pm\text{HCl}}^2/\gamma_{\pm\text{KCl}}) \quad (8)$$

a formula proposed by VALENSI<sup>3</sup> as a general definition of pH in the range of low ionic strengths. If  $\text{K}^+$  or  $\text{Cl}^-$ , or both, are not present in the solution under study small amounts of KCl are added and  $Q_{\text{Cl}^-\text{K}^+}$  is extrapolated to zero molality of KCl. We now suggest that, if  $\gamma_{\pm\text{HCl}}$  and  $\gamma_{\pm\text{KCl}}$  are taken equal to their values in solutions of pure HCl and pure KCl of the same ionic strength as the solution under study, the expression

$$m_{\text{H}^+} = Q_{\text{Cl}^-\text{K}^+}\gamma_{\pm\text{KCl}}/\gamma_{\pm\text{HCl}}^2 \quad (9)$$

could be regarded as a very good approximation for  $m_{\text{H}^+}$ . At higher ionic strengths the same procedure could be applied to each of the  $Q_{ij}$ 's of formula (7) and again a good approximation for  $m_{\text{H}^+}$  should be obtained.

In their report to the I.U.P.A.C. BATES AND GUGGENHEIM<sup>4</sup> consider only quantities of the  $N_i$  type defined in (3), with  $i$  taken as  $\text{Cl}^-$ . We have:

$$N_{\text{Cl}^-} = a_{\text{H}^+}a_{\text{Cl}^-} \text{ and } Q_{\text{Cl}^-} = N_{\text{Cl}^-}/m_{\text{Cl}^-} \quad (10)$$

or

$$a_{\text{H}^+} = Q_{\text{Cl}^-}/\gamma_{\text{Cl}^-} \text{ and } m_{\text{H}^+} = Q_{\text{Cl}^-}/\gamma_{\pm\text{HCl}} \quad (11)$$

They take for  $\gamma_{\text{Cl}^-}$  a Debye-Hückel value given by:

$$\log \gamma_{\text{Cl}^-} = -AI^{1/2}/(1 + 1.5I^{1/2}) \quad (12)$$

in which  $I$  is the ionic strength. The experimental research suggested above would most usefully include a comparison of the  $a_{\text{H}^+}$  values resulting from the two methods of approach, at least at ionic strengths smaller than 0.1 to which the BATES-GUGGENHEIM method is limited and to which our formula (5) may be expected to apply. Also, a comparison of the  $m_{\text{H}^+}$  values derived from (9) and (11) on the basis of the  $\gamma_{\pm\text{HCl}}$  and  $\gamma_{\pm\text{KCl}}$  obtained from solutions of the pure electrolytes would be highly instructive. For ionic strengths larger than 0.1, the BATES-GUGGENHEIM report does not provide any alternative to our proposed definition (7).

#### SUMMARY

Previous suggestions concerning the definition of pH at low and at high ionic strengths are further examined and compared with some aspects of the report on the standardization of pH by BATES AND GUGGENHEIM.

## RÉSUMÉ

Certaines suggestions antérieures concernant la définition du pH aux basses et aux hautes forces ioniques sont examinées plus avant et comparées à certains aspects du rapport sur la standardisation du pH par BATES ET GUGGENHEIM.

*Departments of Chemistry and Chemical Engineering,  
Stanford University,  
Stanford, Calif. (U.S.A.)*

PIERRE VAN RYSSELBERGHE

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<sup>2</sup> D. A. MACINNES, *J. Am. Chem. Soc.*, 41 (1919) 1086.

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### Polarographic limiting currents in the presence of adsorbed reaction products

A good deal of attention has recently been directed towards establishing the influence of surface films on electrode reactions in general, and on polarographic currents in particular<sup>1-3</sup>. One of the more commonly observed features of systems containing an inorganic depolarizer (*e.g.* copper ion) together with a surface active compound (*e.g.* Triton X-100) is a splitting into two steps of the original polarographic step obtained with depolarizer alone. It has been shown that the first of these steps often behaves as a typical kinetic current, in that its magnitude is not at all, or only slightly, dependent on the mercury reservoir height  $h$ <sup>3,4</sup>. Accordingly, it has been postulated<sup>5</sup> that the current corresponding to the first polarographic step is controlled by the rate of penetration of depolarizer through the adsorbed film and the limiting current on this step has been termed a "penetration current".

Many electrode reactions are known in which the product of the reaction is insoluble and forms a film at the electrode surface. The effects of such films are, in general, expected to be similar to those produced by adding a surface active substance to the solution and, in fact, the appearance of a double d.c. step has often been noted<sup>1,6,7</sup>, especially in cases where films of insoluble mercurous salts have been formed anodically. It is of interest to examine the manner in which "penetration currents" in these systems should depend on the mercury reservoir height.

Consider the hypothetical case where the rate of penetration becomes limiting only in the presence of a critical thickness of film of the insoluble reaction product,  $P$ . Since the film thickness varies throughout the drop life due to accumulation of  $P$  at the electrode surface, it is necessary to consider the case where penetration becomes rate limiting just at the end of drop life. Let  $m$  moles of  $P$  be required to give the critical thickness of film on a mercury drop of maximum size, *i.e.* at the end of drop life. For a given capillary, the maximum drop area remains constant at different mercury heads so that the value of  $m$  is independent of both  $h$  and  $t$ , the drop time. The quantity  $N_p$  of reaction product formed during the lifetime of any drop is given (in moles) by:

$$N_p = \frac{\bar{i} t}{nF} \quad (1)$$

where  $\bar{i}$  is the average current (in A) and  $n$  and  $F$  have their usual significance. Any given value of  $N_p$  is, therefore, associated with a constant product of  $\bar{i}$  and  $t$ . It follows that the product of the drop time and average current,  $\bar{i} t$ , needed for the formation of  $m$  moles of  $P$  by the end of drop life is also constant. Thus,

$$\bar{i} t = k \quad (2)$$

Hence, remembering that  $t$  is inversely related to  $h$  to a good approximation, we have:

$$\bar{i} = k' h \quad (3)$$

In other words, the current required to form the critical thickness of film, and hence

also the limiting "penetration current", are *both directly proportional to the mercury head*.

In the case discussed above, penetration is assumed to become rate limiting quite suddenly when the film thickness reaches a critical value. In practice, it can be expected that there is a range of film thicknesses for which the current is controlled by rates of both diffusion and penetration. The  $h$ -dependence should then be intermediate between  $\bar{i} \propto 1/h$  (diffusion control) and  $\bar{i} \propto h$  ("penetration" control).

Several reports of limiting currents with these characteristics appear in the literature. WANG<sup>8</sup> found that a number of common anions gave anodic steps, the heights of which were directly proportional to  $h$ . Even those anions whose mercurous salts were quite soluble gave limiting currents when the rate of production of mercurous ions was sufficiently high for a crystalline film of the salt to form at the electrode surface; a limiting penetration rate through this film then gave rise to the observed step. VLCEK<sup>9</sup> found that the anodic chloride step split into two steps at concentrations greater than about  $2 \cdot 10^{-3} M$ . Examination of his results for variation of mercury head reveals that the first limiting current ( $i_1$ ) has an  $h$ -dependence intermediate between  $i_1 \propto h$  and  $i_1 \propto 1/h$ , indicating that it is probably a penetration current.

It is of importance that limiting currents of the type discussed here depend on  $h$  in the same way as the limiting currents of classical adsorption pre-steps<sup>10,11</sup>, the formation of which is generally believed to occur through an entirely different mechanism. Furthermore, current/time curves of individual drops for limiting currents in the presence of reaction product films<sup>1</sup> show the same initial steep rise and subsequent decay of current as is typical of an adsorption current. Thus both of the criteria commonly employed to characterize adsorption pre-steps may fail to discriminate between an adsorption pre-step produced by the classical mechanism (BRDICKA<sup>10</sup>), and a step resulting from inhibition of the electrode reaction by a product of that reaction. It is also doubtful whether the reversibility or otherwise of the main, diffusion-controlled step is an adequate indication of the mechanism of pre-step formation, as has been suggested<sup>1</sup>. In the cases of methylene blue<sup>12</sup> and riboflavin<sup>13</sup> it has been demonstrated that the film of reductant remains adsorbed at potentials more negative than the pre-step; furthermore, the main step of riboflavin is found to be only slightly reversible in acid solution ( $\text{pH} \leq 1$ )<sup>13</sup> and the reversibility of other main steps associated with classical adsorption pre-steps has never been fully established. It seems desirable, therefore, that the mechanism of pre-step formation be re-examined in order to set up criteria which will unequivocally distinguish between the possible types of electrode processes.

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*Noyes Chemical Laboratory,  
University of Illinois  
Urbana, Ill. (U.S.A.)*

T. BIEGLER

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### Book Reviews

*Methoden der Infrarotspektroskopie in der chemischen Analyse*, by IVO KÖSSLER, Geest and Portig, K. G., Leipzig, 1961, vii + 220 pages, £2. (Translated from Czechoslovakian by Helga Bazantova.)

In spite of the large number of comprehensive publications in the field of i.r. spectroscopy there has been, surprisingly, a need for a good presentation of strictly analytical applications, especially of the various methods of quantitative analysis. Therefore, a systematic survey of this subject, which has been used as a routine method in practical analysis for a long time, is very welcome.

First of all, the origin of i.r. radiation and i.r. spectra of molecules, as well as measuring instruments and their calibration, are treated very concisely. A more detailed discussion of the preparation of samples, which is most important in practice, is followed by a short section on qualitative analysis, *i.e.* identification, testing of purity, and structure determination. The author then gives a detailed discussion of quantitative analysis, in which he describes first the basis (the Lambert-Beer law etc.), then the methods of measurement used in quantitative analysis (compensation, base line, difference of optical density methods and differentiation of spectra), and finally, the reference standards, determination of cell thickness, deviations from the Lambert-Beer law, and the sensitivity and accuracy of analyses. There are detailed discussions of the problems caused by overlapping of characteristic bands used for analysis, recording the time-dependence of spectra for reaction kinetic measurements, and, especially, determination of the integrated absorption and the true optical density and half-band width, which are needed to determine absolute intensities according to D. A. Ramsay. Anyone using KÖSSLER's book to acquaint himself with the techniques of quantitative i.r. analysis, and to learn their possibilities and limitations, will find the clear account of the methods of evaluating the results of analyses very useful, especially the 16 examples taken from the literature and discussed individually. The book ends with short chapters on analytical applications of i.r. spectroscopy in connection with separation methods (consideration of vapour phase chromatography would be useful here), and documentation.

The reviewer would like to suggest, for a second edition, that better spectra should be used, if possible, and that these should always be plotted in the same way. Conforming with general practice, wavelengths should be given in  $\mu$  and the letter  $\epsilon$  should be used for extinction coefficients. For wavelength calibration reference should be made to the IUPAC-publication (*Tables of wave numbers for the calibration of infra-red spectrometers*, Butterworths Sci. Publ., London, 1961). For analysis of binary systems, the very useful method of the isobestic point (H. L. Schläfer, *Angew. Chem.*, 69 (1956) 667) should be mentioned, as well as the paper by Mecke and Mütter (*Z. Elektrochem.*, 58 (1954) 1) for analysing systems having several components with overlapping bands. The value of the book would be further increased if the author compared i.r. analysis with other physico-chemical analytical methods.

KÖSSLER's book is distinguished by a clear presentation and a good selection of material. The descriptions of the various methods are easily understandable, and give all the details required by the reader to choose the method suited to his problem without difficulty, and to familiarize himself with the necessary techniques. This book can therefore be recommended, both as a textbook and a reference book, to anyone who uses i.r. spectroscopy.

W. LÜTTKE, University of Göttingen

*J. Electroanal. Chem.*, 4 (1962) 319

*Physical Properties of Chemical Compounds*, Part III, by R. R. DREISBACH, American Chemical Society, 1961, v + 489 pages, \$ 6.50.

This is the 3rd volume in the *Advances in Chemistry* series, and deals with the tabulation of physical properties of organic compounds. The title of this book is, perhaps, not exact, and could lead to misunderstanding, because the physical properties tabulated are mainly thermodynamic quantities.

It is not easy to understand why the tables include the space and headings for many properties, such as purity, dispersion, ultraviolet and infrared values, etc., for which no numerical data are given, even though they may be available from reliable original literature, or can be found easily in other collections of numerical data, e.g. the *Landolt-Börnstein Tabellen*.

The numerical data for a very important property, i.e. solubility in various solvents, are also not given, so that the final usefulness of these tables is very limited. In addition, the abbreviations given for references are not explained in the text.

*J. Electroanal. Chem.*, 4 (1962) 320

*Thermodynamics*, by G. N. LEWIS AND M. RANDALL, revised by K. S. PITZER AND L. BREWER, 2nd edn., McGraw-Hill Book Co., N.Y. and London, 1961, xii + 723 pages, \$ 12.50 or 97s.

At the time I was a young chemistry student (many years ago) we respected the classical textbook *Thermodynamics* by G. N. LEWIS AND M. RANDALL as the "Bible" for physical chemistry, and, among students, the sentence: "It is in LEWIS AND RANDALL" was always the final word in disputes and discussions to overwhelm the adversaries. In fact, this textbook was so nearly perfectly written for teaching thermodynamics that it is difficult to think of anything better at that time.

But time flows on, not only for men, but also for books, so that the same text, of about forty years ago, could not be used for lectures to-day. It must be recognized that revision of such a text was a tremendously difficult task, and Profs. PITZER AND BREWER have succeeded in maintaining the structure, the ease of reading, the rigour of mathematical treatments, the stringent logic, and, in general, the particular flavour of this book, that made it so welcome at the time it first appeared. They give, at the same time, a text brought entirely up-to-date. It is, perhaps, not particularly interesting to give in detail what has been eliminated and what has been added. Very shortly, the most important additional material concerns the thermodynamical results of statistical mechanics, the use of irreversible thermodynamics, the expansion of the treatment of surfaces, and of gravitational and electromagnetic fields.

A change particularly welcomed for European readers is the adoption of the so-called "European signs" for the electric tensions of individual electrodes, giving the minus sign to the standard electric tension of base metal electrodes, and the plus sign to noble metal electrodes, so that a source of difficulty and of potential confusion has been eliminated.

G. MILAZZO, Istituto Superiore di Sanità, Rome

*J. Electroanal. Chem.*, 4 (1962) 320

*pH Measurement and Titration*, by G. MATTOCK, Heywood and Co. Ltd., London, 1961, xiv + 404 pages, 84 fig., £3 5s.

Each chapter of this book is complete in itself. The first two chapters deal mainly with theory, and the remaining thirteen are more practical. Unusually extensive and up-to-date information is given on various aspects of the glass electrode. The book has many good figures and plates of apparatus and electrodes, including those used in industry.

The last three chapters deal with pH titrations, including automatic titrations. Here, the theory is treated only briefly, and the reader is referred to well-known literature on this subject.

This book will be very useful in the laboratory. Its almost complete lists of references are valuable. By checking, I missed only the tantalum electrode (*Collection Czechoslov. Chem. Commun.*, 16 (1951) 128) which has, in any case, not been accepted in practice.

H. L. KIES, Delft

*J. Electroanal. Chem.*, 4 (1962) 320

## 1. Fundamental electrochemistry

**765 – Theory of dielectrics** (in German). K. E. Slevogt (Institut zur Entwicklung chem. phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Mitt. Inst. Entwickl. chem. phys. Analysenmethoden, Weilheim/Obb.*, II (1961) 25–56.

Ausgehend von der klassischen Resonatoren-Theorie von Drude wird die Frequenzabhängigkeit der dielektrischen Brechung und Absorption berechnet. Bereits Drude konnte zeigen, dass die gleichen Beziehungen erhalten werden, wenn man das Vorliegen eines geschichteten (inhomogenen) Mediums annimmt. Auf den Arbeiten von Maxwell aufbauend beschrieb Wagner das Verhalten inhomogener Dielektrika erschöpfend, wobei er die Erscheinung der dielektrischen Nachwirkung aus den Maxwell'schen Gesetzen ableitete. Abschliessend werden die wichtigsten Zusammenhänge der Debye'schen Dipol-Theorie gegeben, welche die dielektrische Absorption auf eine drehende Reibung kugelförmig gedachter Dipole mit starr eingebautem Dipol zurückführt.

[Fr.Oe.]

**766 – The determination of dipole moments in aqueous solutions** (in German). F. Oehme and M. Feinauer (Institut zur Entwicklung chem. phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Mitt. Inst. Entwickl. chem. phys. Analysenmethoden, Weilheim/Obb.*, 4 (1961) 80–112.

Die klassische Debye-Theorie kann zur Bestimmung von Dipolmomenten nur dann herangezogen werden, wenn die Probe in einem unpolaren und indifferenten Lösungsmittel löslich ist. Im Gegensatz hierzu lässt sich die Onsager-Theorie auch auf polare, nichtassozierte Lösungsmittel übertragen. Noch allgemeiner sind theoretische Ansätze von Buckingham, welcher auf einer modifizierten Kirkwood-Theorie aufbaut und bei assoziierenden Lösungsmitteln ein Korrekturglied für die Abhängigkeit der Molpolarisation des Lösungsmittels von der Konzentration des Gelösten einführt. Die Buckingham-Theorie wird zunächst für Momentbestimmungen von mit Wasser mischbaren organischen Verbindungen bekannten Dipolmomentes herangezogen. Die erhaltenen Momente stimmen im allgemeinen gut mit den in unpolaren Lösungsmitteln bestimmten überein. Anschliessend werden die Momente einiger bisher nicht untersuchter Polyoxyverbindungen gemessen und mit den aus der Konstellation berechneten Werten verglichen. Dieser Vergleich erlaubt besonders bei Verbindungen mit frei drehbaren OH-Gruppen eine Konstellationsaussage.

[Fr.Oe.]

**767 – Theoretical and practical discussions of Cole-Cole diagrams** (in German). F. Oehme (Institut zur Entwicklung chem. phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Mitt. Inst. Entwickl. chem. phys. Analysenmethoden, Weilheim/Obb.*, 3 (1961) 64–74.

Einleitend wird eine knappe Darstellung der Debye-Theorie gegeben und die Gültigkeit der Debye'schen Vorstellungen an Hand von  $\epsilon' = f(\omega)$  sowie  $\epsilon'' = f(\omega)$ -Diagrammen von *n*-Octylbromid geprüft. Abweichungen zur Theorie können durch Einführung einer Verteilungsfunktion der Relaxationszeit korrigiert werden.

Im Gegensatz zu den genannten Funktionen liefern Cole-Cole-Diagramme sehr übersichtliche Bilder, welche speziell auch bei der Untersuchung von Mehrstoffsystemen Aussagen über die zwischenmolekulare Wechselwirkung zulassen.

[Fr.Oe.]

**768 – Extension of Stokes' law for ionic motion to include effect of dielectric relaxation** (in English). R. H. Boyd (Central Research Department, Experimental Station, E.I. du Pont de Nemours and Co., Wilmington, Del., U.S.A.). *J. Chem. Phys.*, 35 (1961) 1281–1283. The purpose of the present paper is to confirm the suggestion made by Fuoss that dielectric relaxation in polar solvents induced by ionic movement gives rise to frictional resistance to that motion.

It is shown that the effect of dielectric relaxation on ionic motion can be treated theoretically on a macroscopic basis in a manner consistent with Stokes' law. The dielectric relaxation times for polar solvents are such that they lead to an effect of the proposed magnitude.

[G.Mar.]

**769 – The properties of international Weston elements on charging and discharging** (in German). M. Froehlich (Physikalisch-Technische Bundesanstalt, Braunschweig, Deutschland). *Z. Instrumentenk.*, 70 (1962) 56–64.

Die in den Elementen mit Hysterese vorhandenen Inhibitoren verursachen beim Laden und Ent-

laden ausser einer höheren Polarisation gegenüber Elementen ohne Hysterese zeitliche Spannungsänderungen in Form von Maxima und Minima. Während sich am Cadmium-Pol sofort nach Einschalten des Stromes eine dem Strom entsprechende konstante Überspannung einstellt, die grösser ist als in den Elementen ohne Hysterese, tritt am Quecksilber-Pol eine hohe, mit der Zeit sich ändernde Überspannung auf. Sie wird auf das durch den fließenden Strom gestörte Inhibitoren-Adsorptionsgleichgewicht an der Elektrode zurückgeführt. Von der Wiedereinstellung dieses Gleichgewichtes hängt die Erholzeit der Elemente beim Laden und Entladen ab. [Fr.Oe.]

**770 – Interfacial solutions of the Poisson–Boltzmann equation** (in English). F. H. Stillinger, Jr. (Bell Telephone Laboratories Inc., Murray Hill, N. J., U.S.A.). *J. Chem. Phys.*, 35 (1961) 1584–1589.

An investigation of a model illustrating only a single aspect of the interfacial structure problem. The form and nature of the non-spherical average potential and charge surrounding a point ion near the solution–substrate interface are analysed.

The relevant solutions to the linear Poisson–Boltzmann equation are obtained as simple quadrature. The present analysis leads to a computation of the reversible work necessary to force the ion atmosphere of an ion to be adsorbed at the substrate–electrolyte interface, into one hemisphere. Implications for ionic adsorption processes are discussed. An analogous procedure is indicated briefly for the case of a point dipole oriented normally to the interface. [G.Mar.]

**771 – The theory of ion pairs in solutions** (in English). J. C. Poirier and J. H. DeLap (Department of Chemistry, Duke University, Durham, N.C., U.S.A.). *J. Chem. Phys.*, 35 (1961) 213–227.

A precise definition of an "ion pair" is considered. It consists of two ions, sufficiently close to each other, each ion being sufficiently far removed from other ions. Ion partners are defined in two ways. For each of the two alternative definitions, distribution functions in the form of integral equations are derived and solved, analytically or numerically, for a variety of systems.

Some thermodynamic properties of the electrolytic solution (association constants, degrees of association, activity coefficients) are determined and discussed. A comparison of distribution functions is made, the usefulness of the ion-pair approach is discussed, and the extension of the present theory is envisaged. [G.Mar.]

**772 – The effect of sinusoidal current on electrode processes. VIII. The effect of alternating current on the intensity of the direct current between two polarised zinc electrodes** (in Hungarian). T. Erdey-Gruz, J. Dévay and R. Szegedi (Institute for Physical and Chemical Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 140–142.

The intensity of the direct current between two polarised Zn electrodes in 5% KCl solution, for the case of the same electric tension, would be increased by alternating current. The increase of the intensity is the higher, the higher the intensity and the smaller the frequency of the alternating current. The electric tension of both electrodes became closer because of the periodic tension fluctuation. Therefore, an increased direct current intensity is necessary to obtain a constant electric tension. [J.Inc.]

**773 – The temperature coefficients of electrode potentials. The isothermal and thermal coefficients and the standard ionic entropy of electrochemical transport of the hydrogen ion** (in English). A. J. de Bethune, T. S. Licht and N. Swenderman (Chemistry Department, Boston College, Chestnut Hill, Mass., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 616–625.

On définit par coefficient de température "isotherme" d'une électrode, la variation  $(dV/dT)_{\text{isoth}}$ , en fonction de la température, de la tension électrique d'une cellule dans laquelle la tension  $V$  de l'électrode est mesurée par rapport à une électrode standard d'hydrogène à la même température. Ce coefficient est directement lié à l'entropie  $\Delta S$  de la réaction. On définit par contre par coefficient de température "thermique" la variation  $(dV/dT)_{\text{th}}$  de la tension, en fonction de la température, d'une électrode mesurée par rapport à une électrode de même espèce mais à température fixée. Ce dernier coefficient est lié à l'entropie  $S^*$  transportée du réservoir de chaleur "chaud" vers le réservoir "froid". L'entropie  $S^*$  est la résultante de deux termes, l'entropie  $S_E^*$  du transport électronique relatif à la réaction d'électrode et l'entropie  $S_M^*$  de migration reliée à la tension électrique de jonction liquide. En supposant cette dernière tension égale à zéro pour un pont de KCl saturé, il est possible d'évaluer  $(dV/dT)_{\text{th}} = +0.871 \text{ mV/}^\circ\text{C}$  pour l'électrode standard d'hydrogène à  $25^\circ$ . A l'aide de cette valeur on détermine les entropies ioniques standard du transport électronique  $S^*_{Ei}$  de l'ion hydrogène ( $S^*_{Ei} = -4.48 \text{ cal/}^\circ\text{C}$ ) ainsi que de n'importe quel ion de charge  $z_i$  ( $S^*_{Ei} = S_i^\circ - z_i$ ) ( $-4.48 \text{ cal/}^\circ\text{C}$ ) où  $S_i^\circ$  représente l'entropie standard mesurée en admettant  $S_i^\circ(\text{H}^+) = 0$ . Les coefficients  $(dV/dT)_{\text{th}}$  sont alors calculés dans le cas de l'électrode au



calomel, au chlorure d'argent et au sulfate de cuivre. On démontre par ailleurs que  $(dV/dT)_{th} - 0.871 \text{ mV}^\circ\text{C} = (dV/dT)_{isoth}$ . Un tableau est présenté comprenant les valeurs  $(dV/dT)_{th}$  et  $(dV/dT)_{isoth}$  pour un grand nombre d'électrodes dans leurs conditions standard à  $25^\circ$ . [H.Hur.]

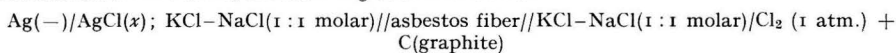
**774 - Salt effect in metal-ammonia solutions. Sodium chloride in sodium-ammonia solution at  $-33^\circ$**  (in English). D. S. Berns, G. Lepoutre, E. A. Bockelman and A. P. Patterson (Sterling Chemistry Laboratory, Yale University, New Haven, Conn., U.S.A.). *J. Chem. Phys.*, 35 (1961) 1820-28.

The authors, using the model of Becker, Lindquist and Alder, and assuming an ionization equilibrium for an added salt, compute theoretically the concentrations of all postulated ionic species in solution, when sodium chloride is added to a sodium-ammonia solution. Using the theory of Onsager and Kim for the conductance at low fields of a mixture of ions, the authors compute the conductances of solutions. These values are compared with some experimental data. [G.Mar.]

**775 - Electromotive force series of metals in fused salts, and activities of metal chlorides in 1:1 molar KCl-NaCl solutions** (in English). S. N. Flengas and T. R. Ingraham (Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada). *J. Electrochem. Soc.*, 106 (1959) 714-721.

Apparent standard electric tensions for the cell:

$M(-)/MCl_n(x_2); KCl-NaCl(1:1 \text{ molar})//\text{asbestos fiber}/AgCl(x_1); KCl-NaCl(1:1 \text{ molar})/Ag(+)$  were measured at temperatures between  $650^\circ-900^\circ$ . The series of electric tensions of metal-metal chlorides ( $M/MCl_n$ ) electrodes so derived is compared with values given by other authors. Any theoretical interpretation of these results makes it necessary to choose an ideal reference standard state. Therefore, the following cell was studied:



It is shown that solutions of AgCl in KCl-NaCl (1:1 molar) may be considered to be ideal over the temperature range  $650^\circ-900^\circ$ , and for the range of concentration from very dilute up to 0.5 molar. Using this property it is possible to establish the activity coefficients, the standard partial molar free energies and entropies of mixing of different metal chlorides in 1:1 molar KCl-NaCl.

[H.Hur.]

**776 - Electrochemical behaviour of hydrogen and propane at temperatures near  $200^\circ$**  (in French). R. Vaucher and Mme O. Bloch (Institut Français du Pétrole Rueil-Malmaison, S et O, Délégation générale à la Recherche Scientifique, Comité de Transformation des Energies, France). *Compt. rend.*, 254 (1962) 3676-3678.

Les auteurs présentent une étude voltammétrique de l'oxydation de l'hydrogène et du propane. Le solvant utilisé est l'acide orthophosphorique à  $200^\circ$ , l'anode est en charbon imprégné de catalyseurs (platine, rhodium, iridium, et palladium). Pour une tension électrique donnée (650 mV/électrode à hydrogène) les intensités relatives à l'oxydation de l'hydrogène sont beaucoup plus élevées que celles relatives à l'oxydation du propane. Les électrodes imprégnées de rhodium, d'iridium ou de palladium permettent l'oxydation de l'hydrogène et non celle du propane qui nécessite la présence de platine associée ou non à celle d'autres métaux (rhodium ou iridium).

[An.Sn.]

**777 - Studies on the behaviour of bivalent salts in aqueous solution. I. Cadmium sulphate** (in English). P. K. Jena and B. Prasad (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 39 (1962) 33-40.

Studies with cells using cadmium sulphate and a mixture of cadmium sulphate and potassium sulphate, with and without liquid junction potential, show the presence of  $Cd^{2+}$ ,  $SO_4^{2-}$ ,  $CdSO_4$  and  $Cd(SO_4)_2^{2-}$ . Dissociation constants

$$\frac{(aCd^{2+})(aSO_4^{2-})}{(CdSO_4)} = K_1 \text{ and } \frac{(CdSO_4)(SO_4^{2-})}{(Cd(SO_4)_2^{2-})} = K_2$$

have been calculated and found to be  $6.8 \cdot 10^{-3}$  and  $4.3 \cdot 10^{-2}$  respectively at  $35^\circ$  for cells without liquid junction potential. A method based on the measurement of activity of sulphate with  $NH_4NO_3$  as salt bridge was found to be fairly reliable for finding  $K_1$  and  $K_2$ . This study also gives an idea of the extent of elimination of the junction electric tension by the various salt bridges.

[R.S.Sa.]

**778 - Study of the decomposition potential of  $MnCl_2$**  (in French). M. Bruneaux, Mme. G. Darmois and S. Ziolkiewicz. *Compt. rend.*, 254 (1962) 3668-3670.

Les auteurs étudient la tension de décomposition de  $MnCl_2$  dans les bains suivants: KCl, NaCl,  $MnCl_2-KCl$ ,  $MnCl_2-NaCl$ ,  $MnCl_2$ . Les électrodes utilisées sont le platine (cathode) et le carbone

(anode). Cette tension de décomposition est voisine de 2.1 V lorsque la concentration de  $MnCl_2$  est environ de 50%  $M$ , et pour une température comprise entre 450–500°. L'influence de la température (de 388°–958°) sur la tension de dépôt d'un mélange de  $MnCl_2$ ,  $NaCl$  et  $KCl$  a également été étudiée. [An.Sn.]

See also abstracts nos. 799, 863, 886, 888, 925, 926, 934.

## 2. Apparatus and accessories

**779 – Report on theACHEMA exhibition 1961. II. Apparatus for chemical and physico-chemical methods** (in Hungarian). E. Pungor and Ö. Kovács (Institute of Inorganic Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Lapja*, 17 (1962) 227–232.

A report is given of the chemical and physico-chemical instruments which were exhibited including balances, ultramicro analytical, gas analytical, distillation, electroanalytical, and optical, apparatus. [J.Inc.]

**780 – Anodic amalgam voltammetry. III. Amalgamated platinum and stationary mercury electrodes** (in German). R. Neeb (Institute of Inorganic and Nuclear Chemistry, University of Mainz, Germany). *Z. anal. Chem.*, 180 (1961) 161–168.

A stationary mercury and an amalgamated platinum electrode are described for use in anodic amalgam voltammetry. The two electrodes offer good sensitivity and reproducibility. [Di.Ciò.]

**781 – The special applications of a new polarographic apparatus** (in German). S. Wolf (Physikalisch-chemisches Laboratorium der Metrohm AG., Herisau, Schweiz). *Z. anal. Chem.* 186 (1962) 87–92.

The polarecord E 261 R may be used, with its auxiliary equipment for a.c. polarographic measurements, for anodic stripping techniques, for chronopotentiometry, for automatic coulometric titrations, and potentiometry. [E.Pun.]

**782 – Comparison of two types of dropping mercury electrodes** (in French). M. J. Bourzeix, Mme. J. Robert and M. L. Viet (C.N.R.S. Laboratoire de Physique-Enseignement, Sorbonne, et Laboratoire de Chimie physique, Ecole de Physique et Chimie, France). *Compt. rend.*, 254 (1962) 3532–3534.

Les auteurs étudient l'influence d'un courant alternatif sur la réduction polarographique du cadmium à une électrode de mercure. Deux types différents d'électrode sont utilisés (1) électrode à gouttes renouvelées H (type Heyrovsky); (2) électrode à goutte pendante K (type Kemula).

On constate que pour les deux types d'électrode les tensions électriques de demi vague  $E_1$  sont indépendantes de l'amplitude et de la fréquence du courant surimposé (de 1–100  $\mu A$  et de 3–10.000 Hz). Pour l'électrode H ces paramètres sont également sans influence sur la valeur du courant limite de diffusion  $i_a$ , alors qu'ils influencent notablement le courant de pic  $i_p$ , obtenu avec l'électrode K. Cette étude a permis de choisir les conditions d'amplitude et de fréquence du courant alternatif permettant de déterminer les composantes de l'impédance,  $Z = R - j/c\omega$ , d'une cellule comprenant une électrode de mercure (type H ou K) et une électrode de platine de 8  $cm^2$  de surface. [An.Sn.]

**783 – A portable, dissolved-oxygen indicator** (in English). R. Briggs and W. H. Mason (Water Pollution Research Laboratory, Stevenage, Herts., England). *Lab. Practice*, 11 (1962) 36–44.

A robust and portable instrument for routine dissolved-oxygen determinations is described. This instrument may be used to study the respiration of tissues and for the aeration and de-aeration of polluted rivers. It indicates the dissolved-oxygen concentration in liquids as parts per million by weight, and incorporates a wide-bore dropping mercury electrode, which is maintained at 1.5 V negative to a silver-silver chloride comparison electrode. Temperature compensation is provided. [Di.Ciò.]

**784 – A simple column of high efficiency for high voltage electrophoresis** (in German).



G. Rentsch (Victor von Scheffelstrasse 2, Bamberg, Deutschland). *Biochem. Z.*, 335 (1961) 69-74.

A column is described in which the electrodes are provided with a cooling system. This permits the use of voltages up to 100 V. The column enables amounts of the order of one gram to be separated. [Gio.Ser.]

**785 - Micro-electrophoresis on starch gels** (in French). H. Mouray, J. Moretti and J. M. Fine (Laboratoire de chimie biologique, 45 rue St. Pères, Paris, France). *Bull. soc. chim. biol.*, 43 (1961) 993-1003.

A technique and apparatus are described for the electrophoretic separation of small amounts (5-10  $\mu$ l) of protein solutions on starch gel. The time required for one separation is 2 h. The effect of the gel preparation, the buffer and the current on the separation is discussed. [Gio.Ser.]

**786 - An automatic coulometric-titration assembly** (in English). P. G. W. Scott and T. A. Strivens (Instrumentation Laboratory, W. G. Pye & Co. Ltd., Cambridge, Great Britain). *Analyst*, 87 (1962) 356-361.

Titration takes place at approximately constant current, and a commercial integrating amplifier is used to integrate the current-time curve. Use of a potentiometric end-point indicator permits the use of the usual titrator-controller to decrease the current near the end-point. Integrator output is recorded as a bar presentation. The apparatus was tested by titrations of  $K_2Cr_2O_7$  with electro-generated  $Fe^{2+}$ , and of  $Cl^-$  with electro-generated  $Ag^+$ . 2 mg of Cr could be determined with a standard deviation of  $\pm 0.18\%$  and 0.02 mg with a standard deviation of  $\pm 1.27\%$ . 3.6 mg of  $Cl^-$  could be determined with a standard deviation of  $\pm 0.17\%$  and 0.2 mg with a standard deviation of  $\pm 4.65\%$ . [P.O.Ka.]

**787 - An automatic coulometric titrimeter** (in English). K. Jeffcoat and M. Akhtar (Courtaulds Limited, Coventry, Warwickshire, Great Britain). *Analyst*, 87 (1962) 455.

This is an apparatus with an externally generated titrant for acid-base titrations. It is completely automatic with a sequence controller which controls the following steps: (a) solution from a previous titration is removed from the titration cell; (b) a sample ( $\sim 0.5$  ml) is taken, diluted with ca. 100 ml of a suitable liquid and transferred to the cell; (c) the solution for generating titrant is delivered to the cell; (d) the coulometric cell current, the integrator for this current and a stirrer in the titration cell are switched on; (e) when the pH of the cell solution (measured by a glass-calomel electrode system and a E.I.L. pH meter) reaches a pre-set value near the end-point, the coulometric current is reduced to one seventh of its normal value; (f) when the pH reaches the end-point the coulometric current is switched off but the reagent pump is operated for 15 sec more to flush titrant from the cell; (g) the current-time integral is converted to an equivalent electric tension and recorded on a potentiometric recorder; (h) all controls are re-set for the next titration. The maximum rate of analyses is 12/hour, and an accuracy of  $\pm 0.2\%$  of full-scale deflection can easily be achieved. [P.O.Ka.]

**788 - The Philips conductivity bridge PR 9501** (in German). *Z. Instrumentenk.*, 70 (1962) 51.

Die direkt anzeigende Leitfähigkeitsmessbrücke arbeitet mit einer wählbaren Messfrequenz von 80 oder 1000 Hz, je nach Messbereich und Zellenkonstante. Die Brücke misst das Verhältnis eines unbekanntes Widerstandes  $R_a$  zu einem bekannten Widerstand  $R_b$ .  $R_b$  kann dabei mit Hilfe eines 11-stufigen Umschalters verändert werden. Durch eine Gegenkopplung erhält der Anzeigeverstärker eine Spannung, welche dem Verhältnis  $R_b/R_a$  proportional ist. Mit einer besonderen Schalterstellung kann das Gerät mit erhöhter Empfindlichkeit für konduktometrische Titrations eingesetzt werden. [Fr.Oe.]

**789 - Use of permanganometry in automatic instruments** (in German). G. Halfter and W. Kuttler (Analytisches Laboratorium, Fa. Geigy A. G., Grenzach/Baden, Deutschland). *Z. anal. Chem.*, 176 (1960) 111-115.

The use of an automatic titrating instrument for permanganometry is described. [Di.Ciò.]

**790 - Behaviour of simple electrodes in potentiometric determinations of acid-base titrations** (in English). T. M. Salem and S. A. Awad (Ain Shams University, Egypt). *J. Indian Chem. Soc.*, 39 (1962) 141-142.

Cadmium, tin and tin amalgam electrodes were tried in media at pH values higher than 7 for titrating strong alkali with strong and weak acids, such as hydrochloric, sulphuric, phosphoric, citric and acetic acids, and it was shown that these electrodes can be used as indicator electrodes in acid-base titrations. [R.S.Sa.]

**791 - The use of uncalibrated dropping capillaries for routine polarographic determinations**

(in English). J. L. Flounders (Electrolytic Zinc Co., Risdon, Tasmania, Australia). *Lab. Practice*, 11 (1962) 209-210.

The author described the equipment used and the method whereby dropping capillaries, having almost any properties, may be used with a standard polarograph without recalibration. [Di.Ciò.]

See also abstracts nos. 769, 788, 800, 885, 902, 924.

### 3. Polarography

**792 - The effect of residual current and cell resistance in current scanning polarography and its application to simultaneous determination of two substances** (in Japanese). K. Izutsu (Chemistry Institute, Faculty of Science, University of Kyoto, Sakyo-ku, Kyoto, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1500-1503.

Fundamental studies on current scanning polarography at the D.M.E. were carried out, for the following: (1) residual current: In a solution where only a supporting electrolyte ( $O_s$ ) is present, the residual current coincides, both experimentally and theoretically with the average residual current found in conventional polarography. However, in the presence of reducible substance ( $O_1$ ), the residual current ( $i_r'$ ) to be corrected at the electric tension ( $E'$ ) where the limiting current of  $O_1$  is measured, is not equal to the current ( $i_r$ ) at  $E'$  in the absence of  $O_1$ . Theoretical considerations of the charging current showed that  $i_r'$  is approximately equal to  $(2/3)i_r$  when  $O_s$  is irreversible, and to  $(9/10)i_r$  when  $O_s$  is reversible; (2) simultaneous determination of two substances: In the case when two reducible substances  $O_1$  and  $O_2$  are present, their limiting currents are influenced by the reversibility of the electrode reaction of  $O_2$  and  $O_s$ . However, by applying the relations derived in the previous paper (cf. K. Izutsu, *ibid.*, 82 (1961) 703), the concentrations of  $O_1$  and  $O_2$  could be calculated from the limiting currents obtained experimentally; (3) effect of cell resistance: The polarogram is hardly distorted by the high resistance of the cell circuit. Therefore, this method seems to be especially useful for polarography in non-aqueous solvents. [Ta.Fu.]

**793 - Some abnormal phenomena in current scanning polarography** (in Japanese). K. Izutsu (Chemistry Institute, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1503-1506.

Polarographic phenomena such as maxima, minima, migration currents, oxidation currents, mixed electric tensions, kinetic currents, catalytic currents, and adsorption waves were investigated by current scanning polarography at the dropping mercury electrode, and they were compared with those obtained by conventional methods. The behavior of the current-electric tension curves for these phenomena are almost the same in the current scanning as in the conventional method, but maxima do not appear in the current-electric tension curves. Limiting kinetic current curves were derived by taking into account the irreversibility of the electrode reaction of the substance reduced at a more negative electric tension. In order to derive these equations, the relations derived by Matsuda and Ayabe (*Bull. Chem. Soc. Japan*, 28 (1955) 422; 29 (1954) 134) for kinetic current in the conventional method were applied. [Ta.Fu.]

**794 - Instrumentation and theoretical considerations for a microanalytical method using potential step voltammetry** (in Japanese). S. Oka (Shimadzu Seisakusho Ltd., Nakakyo-ku, Kyoto, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1202-1206.

An electrochemical method is described for trace analysis, in which the electric tension of a working electrode, initially at its equilibrium value, was abruptly changed, and the induced current through the cell was observed by means of a synchronized oscilloscope. The hanging mercury drop electrode was used as the working electrode, and the drop was renewed after each reading for the current-time curve. The current-electric tension curve is obtained from the plot of the values of current at a finite time  $t_1$  (as soon as  $5 \cdot 10^{-4}$  sec after the electrolysis begins) against the various applied electric tensions. Control of electrolysis voltage within 3 mV, and transient response to changes occurring as quickly as  $2 \cdot 10^4$ /sec were attained by an electronic potentiostat. The resulting current-electric tension curves were similar to those obtained from the ordinary d.c. polarograms. In this method, however, the residual currents are completely eliminated, and the magnitudes of the limiting currents in which the time of duration  $t_1$  is  $5 \cdot 10^{-4}$  sec is about 70 times larger than that in ordinary polarography using a dropping mercury electrode, whose drop time is about 5 seconds,

even if the electrode area is the same in both methods. Theoretical considerations for this method and experimental results for the electrode reduction of cadmium ions are also presented. [Ta.Fu.]

**795 – A new fast-polarograph** (in German). K. Kronenberger and W. Nickels (Abteilung M.A.T. der Atlas-Werke AG., Bremen, Deutschland). *Z. anal. Chem.*, 186 (1962) 79–85. Measurement of polarographic currents before the mercury drops fall has the following advantages: (1) the sensitivity is twice that achieved in normal polarography; and (2) the disturbing effect of the capacitative current decreases. The new fastpolarograph "Selector V" offers the advantage of measuring only points in the  $i-V$  diagram, because the electrode electric tension governs the recording system. In order to eliminate the deleterious effect on the electrode surface, the current may be measured on every second drop. [E.Pun.]

**796 – The effect of experimental conditions in square-wave polarography using anodic stripping techniques before analytical determination** (in German). F. v. Sturm and M. Ressel (Forschungslaboratorium der Siemens-Schuckertwerke AG., Erlangen, Deutschland). *Z. anal. Chem.*, 186 (1962) 63–79.

Die anodische Stufe einiger Elemente wurde an der hängenden Quecksilberelektrode nach Vor-elektrolyse untersucht. Die Elektrolyse findet in 0.1–0.5 M Grundelektrolyt an einer Hg-Oberfläche von 1–1.5 mm<sup>2</sup> zwei bis zehn Minuten lang statt. Die Rechteckwellenpolarographie wird in Abwesenheit von Sauerstoff und oberflächenaktiven Substanzen benützt. Nur die reversiblen Elektrodenvorgänge sind gut verwendbar, so dass die Möglichkeit der Bestimmungen nur auf ungefähr 15 Elemente beschränkt ist.

Die anodische Stufe ( $i_p$ ) wächst mit der Rührgeschwindigkeit der Lösung ( $u$ ).

$$i_p = k_1 + k_2\sqrt{u}$$

Im Falle der irreversiblen Elektrodenreaktion wird  $i_p$  durch fremde Elektrolyte besonders durch den  $N(CH_3)_4^+$ -Ion und durch die Anwesenheit kapillaraktiver Stoffe vermindert werden.

Auf die von Kemula entdeckten Intermetallen-Bildungen, welche eine Erniedrigung der Stufen verursachen, wurde die Aufmerksamkeit gelenkt. Die Bestimmungsgrenzen liegen bei 4 ng Tl, 1.2 ng Pb, und 0.2 ng Cd in Mikrozelle. Die wichtigsten Daten der bestimmbareren Elemente (Bi, Cu, Sb(III), Pb(II), Sn, Tl(I), Cd, In, Zn, Mn und Ba) sind tabellarisch zusammengestellt. [E.Pun.]

**797 – The growth of the sensitivity of a.c. polarography** (in German). R. Neeb (Institute of Inorganic and Nuclear Chemistry, University of Mainz, Germany). *Z. anal. Chem.*, 186 (1962) 53–63.

Die Empfindlichkeit der Wechselstrompolarographie erhöht sich, wenn der Oberwellenanteil des angewandten sinusförmigen Wechselstromes an Stelle der Grundwelle gemessen wird. Das Verfahren beruht auf der Tatsache, dass die Oberwellen im Falle des kapazitiven Stromes nicht entstehen können, aber im Falle der elektrochemischen Vorgänge hergestellt werden. Das beschriebene Gerät ermöglicht eine selektive Verstärkung der Oberwellen. Die Empfindlichkeit vergrößert sich mit der Anwendung von pseudostationärer an Stelle von tropfender Quecksilberelektrode. ( $t$  ist ungefähr gleich mit 34 sec, Geschwindigkeit der Gleichspannungsänderung 12.5 sec/V, Registrierpapiergeschwindigkeit ca. 1 m/min, Konzentrationsempfindlichkeit unter 1  $\mu$ g/ml.) [E.Pun.]

**798 – Modern methods in d.c. polarography** (in German). H. W. Nürnberg (Max Planck-Institut für Eisenforschung, Düsseldorf, Deutschland). *Z. anal. Chem.*, 186 (1962) 1–53. A review with 110 references. [E.Pun.]

**799 – Effects of streaming on voltammetric data** (in English). J. W. Olver and J. W. Ross (Department of Chemistry, University of Massachusetts, Amherst, Mass., U.S.A.). *Anal. Chem.*, 34 (1962) 791.

The study examined the effects of streaming on data obtained by several voltammetric methods. Chronopotentiometric techniques at the mercury pool electrode and the hanging drop electrode are included. Results for reduction with controlled current polarography, for rapid potential scan at a hanging drop, and for chronopotentiometry at a hanging drop and a pool cathode are discussed. Convective streaming can very markedly affect data obtained in any of the techniques investigated. For analytical applications, streaming must be eliminated by addition of a suitable maximum depressor. The geometry of the electrode plays some role in the phenomenon of streaming. An important factor is the current density. A certain minimum current density seems necessary to provide motion of the solution. [Kl.Gr.]

**800 – Voltammetric reduction of acids in liquid ammonia** (in English). R. N. Hammer and J. J. Lagowski (Michigan State University, East Lansing, Mich., U.S.A.). *Anal. Chem.*, 34 (1962) 597.

The reduction reactions at a rotating platinum electrode, in liquid ammonia solutions of weak acids containing the ammonium ion, were studied in detail. The reduction wave occurring results from the reduction of ammonium ions and ion aggregates containing this ion. The influence of rotation and temperature is discussed. The relationship between limiting current and concentration of the ammonium ion indicates a diffusion controlled reaction. A dark deposit on the cathode was identified as divided platinum. The arrangement of apparatus and the preparation of the solvent are described. Some voltammetric curves are shown. [Kl.Gr.]

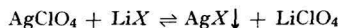
**801 – Inverse polarography and voltammetry. A new method for trace analysis** (in German). R. Neeb (Institute of Inorganic and Nuclear Chemistry, University of Mainz, Germany). *Ang. w. Chem.*, 74 (1962) 203–213.

Es wurde ein Überblick über die Verfahren der inversen Polarographie und Voltammetrie gegeben. Beiden behandelten Verfahren wird das zu bestimmende Ion vor der Bestimmung an einer Arbeitselektrode elektrolytisch angereichert und nachher unter Stromumkehrung findet mit vergrößerter Strom der elektrochemische Bestimmungsvorgang statt. Die Bestimmung kann mit den bekannten polarographischen, voltammetrischen, oscillographischen oder mikroculometrischen Verfahren durchgeführt werden. Mit den Methoden lassen sich noch Analysen in  $10^{-9}$  g Bereich ausführen. Es wurde ferner über die anwendbaren Einrichtungen, Quecksilberelektroden, Metallelektroden, berichtet.

Die Elektrolyse wird unter Umrühren mit einer Spannung, die mit 0.2–0.3 V negativer als die Halbstufenpannung ist, durchgeführt. Bei dem Auflösungsvorgang benutzt man am häufigsten das voltammetrische Verfahren. Liegen mehrere Metalle in der Analyse vor, so entstehen bei der anodischen Wiederauflösung mehrere Spitzen, sofern ihre Spannungsunterschiede wenigstens 0.1 V betragen. Genaue Resultate kann man mit Eichkurven erhalten. (61 Zitaten.) [J.Inc.]

**802 – Voltammetric study of the Ag↓/Ag(I) system in anhydrous tetrahydrofuran** (in French). J. Badoz-Lambling and M. M. Sato (Laboratoire de Chimie analytique, Ecole Supérieure de Physique et Chimie industrielles, 10, rue Vauquelin, Paris, France). *Compt. rend.*, 254 (1962) 3354–3356.

Les auteurs présentent une étude voltamétrique du système Ag ↓/Ag(I) dans le tétrahydrofur anhydre en présence de perchlorate de lithium (0.3 M) comme électrolyte indifférent. L'oxydation anodique de l'argent en présence de chlorure ou de bromure de lithium se traduit par une courbe  $i = f(E)$  présentant un palier limite de diffusion proportionnel à la concentration de l'halogénure. Les systèmes Ag ↓/AgClO<sub>4</sub> et Ag ↓/AgX↓ sont rapides (X = Cl, Br). La constante  $K = (AgClO_4)/(LiX)/(LiClO_4)$  relative à la réaction



est calculée; soit  $pK_{Cl}$  ≠ 16.5 et  $pK_{Br}$  ≠ 19.

[Bad.Lam.]

**803 – Polarographic determination of potassium in a catalyst for isobutyl alcohol synthesis** (in Russian). Ya. I. Tur'yan and V. F. Romanov. *Khim. Prom.*, (1961) 68.

The catalyst is dissolved in 10% HCl, diluted twofold and 15 ml of ethanol are added to 5 ml of the solution. The resulting solution is heated to reduce Cr(VI) to Cr(III), and diluted to 100 ml. 10 ml of this solution are neutralised with 10% tetramethylammonium hydroxide (phenolphthalein), filtered to remove Zn(OH)<sub>2</sub> and Cr(OH)<sub>3</sub>, and after addition of 5 ml of 10% tetramethylammonium hydroxide, diluted to 100 ml. An aliquot of this solution is deaerated and polarographed using a mercury–tetramethylammonium iodide comparison electrode. The quantitative determination is made by the method of standard additions, with an error of 3%. The whole procedure requires three hours, and the results are in agreement with the determination of K by the radiometric method. [Gio.Ser.]

**804 – The reduction waves of copper and lead ions in potassium bicarbonate solution** (in Japanese). H. Shirai (Institute of Industrial Science, University of Tokyo, Chibashi, Chiba, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1179–1182.

From a study of the peak electric tension shift and the concentrations of bicarbonate and hydroxyl ions, copper and lead ions were found to exist in the form of coordinated compounds,  $(Cu(OH)_2(HCO_3)_2)^{2-}$  and  $(Pb(OH)_2(HCO_3)_2)^{2-}$ , respectively, in a potassium bicarbonate solution, whose concentration lies between 0.5–1 M, and the pH between 8.8–10. [Ta.Fu.]

**805 – Polarographic studies on the threoninate complex of copper** (in Japanese). M. Matsuoka (Osaka Works, Tanabe Pharmaceutical Co., Higashiyodogawa-ku, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1036–1038.

The polarographic behaviour of complex cupric ions formed in the presence of excess threoninate ions was studied by means of the dropping mercury electrode. As in the cases of glycinate and alani-

nate, the complex cupric ions were likely to exist as  $\text{CuT}_2$ ,  $\text{CuT}_3^-$  or  $\text{CuT}_4^{2-}$ : *i.e.*,  $\text{CuT}_2$  in the presence of 0.003–0.045 *M* threoninate and 0.0005 *M* cupricion,  $\text{CuT}_3^-$  in the presence of 0.105–0.3 *M* threoninate, and  $\text{CuT}_4^{2-}$  in the presence of 0.495–0.9 *M* threoninate. The dissociation constants of the above complexes were  $2.55 \cdot 10^{-15}$ ,  $1.14 \cdot 10^{-16}$  and  $2.99 \cdot 10^{-17}$ , respectively. [Ta.Fu.]

**806 – Rapid determination of zinc in biological materials** (in German). H. Keller and W. Grashoff (Institut für physiologische Chemie und Physikochemie, Universität Kiel, Deutschland). *Hoppe-Seyler's Z. physiol. Chem.*, 318 (1960) 278–280.

A rapid polarographic method of zinc determination in biological materials, by a modification of the Weitzel-Fretzdorff method, is described. It is possible to determine 5  $\mu\text{g}/\text{ml}$  of zinc. Calcium and phosphate ions do not interfere.  $\text{Fe}^{3+}$  can also be determined. [Di.Ciò.]

**807 – Microanalysis of some metallic ions using potential-step voltammetry** (in Japanese). S. Oka (Shimadzu Seisakusho Ltd., Nakakyo-ku, Kyoto, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1206–1208.

The experimental results of trace analysis of  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Tl}^+$  ions by a new method (*cf.* Oka, *ibid.*, 82 (1961) 1202–1206) are described. Limiting currents and diffusion coefficients for these metallic ions are in good agreement with those calculated theoretically. The sensitivity of trace analysis is 500 or more times greater in the present method than in the ordinary d.c. polarographic method, conceivably because of the elimination of residual currents and the increase of limiting currents. The variation of half-wave electric tensions is also discussed. [Ta.Fu.]

**808 – Effect of the nature and concentration of the supporting electrolyte on the half-wave potential and diffusion current. I** (in English). S. N. Mukherjee and Mrs. A. Chakravarti (Jadavpur University, Calcutta, India). *J. Indian Chem. Soc.*, 38 (1961) 995–997.

The effect of varying the nature and concentration of the supporting electrolyte on the half-wave electric tension and diffusion current of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  as reducing ions was studied. The value of  $i_d$  increases with increasing KCl concentration; it remains constant in the cases of  $\text{KNO}_3$  and  $\text{NH}_4\text{Cl}$ . The half-wave electric tension shows a slight increase with increasing concentrations of KCl,  $\text{NH}_4\text{Cl}$  and HCl in the case of  $\text{Cd}^{2+}$ , but in the case of  $\text{Zn}^{2+}$ , all the three electrolytes showed almost constant  $E_{1/2}$  at all concentrations. An attempt was made to correlate these data with viscosity, but such a correlation was not always found to be possible. In some cases the possibility of complex formation is suggested. [R.S.Sa.]

**809 – Polarographic analyses of cadmium(II), cobalt(II), copper(II), zinc(II), iron(III), tin(IV) and chromium(VI) in acid cyanide gold-plating solution** (in English). J. A. Miller (Instrumentation Laboratory, Boeing Airplane Co., Aeroplane Space Division, Seattle, Wash., U.S.A.). *Plating*, 48 (1961) 1110–1113.

Organic matter is removed from the samples by heating with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ; Au is removed by filtration and the filtrate adjusted to pH 7.  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  are determined in an aliquot using 2 *M* acetic acid–2 *M* ammonium acetate as supporting electrolyte, the half-wave electric tensions being  $-0.07$  V,  $-0.8$  V and  $-1.1$  V vs. a mercury pool anode, respectively. Ni interferes with the Zn determination.  $\text{Fe}^{3+}$  is determined in 2 *M* Na acetate–0.1 *M* EDTA,  $\text{Cr}^{6+}$  in 1 *M* NaOH,  $\text{Co}^{2+}$  in 0.1 *M* KCl (pH 7), and  $\text{Sn}^{4+}$  in 4 *M*  $\text{NH}_4\text{Cl}$ –1 *M* HCl. The half-wave electric tensions are  $-0.1$  V,  $-0.5$  V,  $-1.4$  V and  $-0.5$  V, respectively. [Gio.Ser.]

**810 – Amperometric determination of thallium using cerium sulphate** (in English). D. Singh and V. S. Agarwal (Banaras Hindu University, Varanasi, India). *J. Sci. Ind. Research (India)*, 21 B (1962) 212–214.

Thallium was determined amperometrically in 2 *N* HCl medium at 70°, by titrating against standard cerium sulphate solution. Two polarised electrodes were used at a constant voltage. The method has the advantage of simplicity of technique, and that it permits the estimation of small quantities of thallium (0.2 mg). As, Bi, Cd, Cr(III), Cu(II), Fe(III), Hg (II), Pb, Sb(V), Se, Sn(IV), Te and Zn do not interfere with the determination. [R.S.Sa.]

**811 – Polarographic determination of lead, copper, cadmium and zinc in minerals** (in Russian). M. Ionescu and G. Susman. *Rev. chim. (Bucharest)*, 11 (1960) 589–591.

The polarographic determination of lead, copper, cadmium and zinc, containing also Fe, As, Sb, Bi, Al, Mg, Ca,  $\text{SiO}_2$  is described. 1 *M* ammonium acetate solutions for Pb and Cd determination and 4 *M* ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ ) solutions for Cu, Cd and Zn determination are used. The cathodic polarizations are: 0.2–0.5 V for Pb; 0.4–0.7 V for Cd; 0.0–0.6 V for Cu; and 1.0–1.7 for Zn. [Di.Ciò.]

**812 – Square-wave polarography with special reference to the analysis of zirconium and**

**hafnium** (in English). D. F. Wood and R. T. Clark (Imperial Metal Industries (Kynoch) Limited, Witton, Birmingham, Great Britain). *Analyst*, 87 (1962) 342-348.

Polarographic data, obtained with a Mervyn-Harwell square wave polarograph, are presented for fifteen different metal ions likely to be present as impurities in Zr metal and its alloys. A variety of supporting electrolytes was examined. Zr was added to the solutions to check for interference and it was found that under suitable conditions Cu, Pb, Mo, W and Zn can be determined in Zr based materials by direct polarography, 45 minutes being required for any given metal. Similar experiments showed that Cu, W and Cd can be determined in Hf, after simple solution of the sample. [P.O.Ka.]

**813 - Polarography of divalent tin in sodium formate** (in English). G. S. Deshmukh and V. D. Kane (Banaras Hindu University, Varanasi, India). *J. Sci. Ind. Research (India)*, 21B (1962) 235.

A study of the polarographic behaviour of divalent tin in sodium formate solutions has shown that well developed anodic and cathodic waves are recorded in the pH range 3-4. As the diffusion current is proportional to the concentration of tin upto  $4 \cdot 10^{-4}$  g, the use of sodium formate as a supporting electrolyte in the determination of tin is indicated. [R.S.Sa.]

**814 - Square-wave polarographic behavior of tin and lead in aqueous solutions of citric acid** (in Japanese). H. Hirata and T. Amemiya (Research Department, Wireless Division, Matsushita Electric Ind. Co., Ltd., Kitakawachi, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1285.

The square wave polarographic peak of  $Pb^{2+}$  ion occurs at  $-0.70$  V (vs. Hg pool) in 1 M solutions of citric acid, and that of stannous ion appears at  $-0.26$  V (peak I). When oxygen is dissolved in the solution, the latter peak disappears and at the same time new peaks, II ( $-0.56$ ) V and III ( $-0.86$ ) V appear, which are due to stannic ion. Peaks II and III are far less sensitive than peak I. Coexistence of  $Sn^{2+}$  and  $Pb^{2+}$  gives rise to two peaks at  $-0.29$  V ( $Sn^{2+}$ ) and  $-0.21$  V ( $Pb^{2+}$ ) in 1 M citric acid solution. The sensitivities of the peaks are comparable, so these ions can be determined from the same polarogram.

In the case of  $Sn^{4+}$  and  $Pb^{2+}$ , however, the tin wave is so insensitive that  $Pb^{2+}$  ion (0.02 mg/ml) can be determined from solutions containing 60 times as much stannic ion as  $Pb^{2+}$  ion. [Ta.Fu.]

**815 - The use of sulfonated tolyl and xylol stearic acids as polarographic maxima suppressors** (in English). W. V. Malik and R. Haque (Department of Chemistry, Aligarh Muslim University, Aligarh, India). *Z. anal. Chem.*, 180 (1961) 425-429.

The authors describe the effect of sulfonated tolyl and xylol stearic acids (STSA and SXSA, respectively) on the polarographic waves of  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , a Cu-biuret complex, a Cu-glycine complex, an iodide-cadmium complex and  $Ni^{2+}-Co^{2+}$  mixtures. It was found that STSA and SXSA could be employed as maxima suppressors for the cathodic waves of the ions cited. The P.M.P. values of STSA were found to be greater than those for SXSA; this behaviour may be attributed to the greater effect of the xylol group. [Di.Ciò.]

**816 - Amperometric determination of cerium and iron** (in English). D. Singh and A. Varma (Electrochemical Laboratory, Banaras Hindu University, Varanasi, India). *Current Sci. (India)*, 30 (1961) 137-138.

Ce and Fe can be titrated amperometrically with ascorbic acid at  $50^\circ$  in 2.5 M  $H_2SO_4$  using a rotating Pt electrode at  $+0.36$  V vs. the S.C.E. At higher acid concentrations it is possible to titrate Ce alone, because Fe is not reduced by the ascorbic acid. After the reduction of Ce, the solution is neutralised with aqueous  $NH_3$ , heated at  $60^\circ$  for 5 min, adjusted to pH 1.5, and Fe is titrated without an applied voltage until the cathodic current is zero. The error is less than 2%. [Gio.Ser.]

**817 - A.c. polarographic determination of thorium with copper ethylenediaminetetraacetate** (in Japanese). M. Kodama (Department of Chemistry, Faculty of Arts and Sciences, Ibaraki University, Mito-shi, Ibaraki, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1208-1211.

A.c. polarographic titration of Th in the presence of rare earths (Ce and Nd) was carried out using Cu(II)-EDTA in monochloroacetate buffer at pH 3.0. To eliminate the interference of ceric ion, hydroxylamine hydrochloride or ascorbic acid was added to the solution. End-points were determined by plotting the peak currents of the a.c. polarograms of liberated copper against the volume of Cu(II)-EDTA solution added. The experimental end-points agreed satisfactorily with the stoichiometric equivalence points in the concentration range of  $5 \cdot 10^{-5}$  to  $1 \cdot 10^{-3}$  M.

This method was successfully applied to the determination of Th in monazite sand. [Ta.Fu.]

**818 - Polarographic method for determining nitrate in soil** (in English). G. W. Skyring, B.



J. Carey and V. B. D. Skerman (University of Queensland, Australia). *Soil Sci.*, 91 (1961) 388-392.

A suitable amount (50 g) of soil was extracted with 0.01-0.04 *M* BaCl<sub>2</sub> for 15 min, and filtered. An aliquot (5-10 ml) of the extract was diluted to 25 ml, after addition of 2 ml of zirconyl chloride (8.58%). After deaeration, the diffusion current was measured at -1.16 V. The method was suitable for soils containing only small amounts of gypsum. Cl did not interfere. [Gio.Ser.]

**819 - Amperometric determination of vanadium as vanadyl selenite** (in English). G. S. Deshmukh, O. P. Asthana and V. S. N. Pillai (Division of Analytical Chemistry, Banaras Hindu University, Varanasi, India). *Z. anal. Chem.*, 185 (1962) 429-434.

Vanadium can be determined amperometrically by titrating a vanadium solution against a solution containing a known amount of selenous acid in 0.044 *M* ammonium acetate, in 50-55% alcohol-water solution, having a pH between 5.3-5.5. A tension of -1.10 V vs. S.C.E. is applied to the mercury dropping electrode. The solution must be deaerated before the determination by passing purified nitrogen for 10 min. The precipitating reaction gives a V-shaped curve. The composition of the precipitate was found to be VOSeO<sub>3</sub>. The reverse titration gives no good results. [E.Pun.]

**820 - The determination of traces of antimony, copper and lead in ferro-manganese with a cathode ray polarograph** (in English). A. G. C. Morris (Feralloys Ltd., P. O. Box No. 21, Cato Ridge, Natal, South Africa). *Analyst*, 87 (1962) 478-484.

(a) *Copper and lead*. 1 g of sample was dissolved in 10 ml of 1 : 1 HNO<sub>3</sub>/H<sub>2</sub>O, evaporated to dryness, and the mixed nitrates were decomposed at 500 ± 20° for 3-4 min. The oxides were dissolved in 10 ml boiling concentrated HCl, from which traces of Cu and Pb had been removed by ion exchange. This solution was evaporated to dryness and the residue re-dissolved in 25 ml water plus 5 ml NH<sub>2</sub>OH.HCl solution (10% w/v), and this solution was boiled until it was colourless. It was cooled and diluted quantitatively to 50 ml. 5 ml was taken for polarography, using starting tensions of -0.05 V for Cu and -0.20 V for Pb, measuring at -0.30 and -0.50 V, respectively. Calibration was by standard addition to the final solution.

(b) *Antimony*. 1 g of sample was dissolved in 10 ml of hot 1 : 1 HNO<sub>3</sub>/H<sub>2</sub>O. 20 ml water and 10 ml concentrated HNO<sub>3</sub> were added. The solution was boiled and 2 g KClO<sub>3</sub> were added. Boiling was continued until 2 min after a black precipitate formed. The supernatant liquid was removed with a No. 3 porosity filter stick, the precipitate was washed with 6 × 30 ml cold H<sub>2</sub>O, and dissolved in 25 ml hot concentrated HCl. After cooling, the solution was quantitatively diluted to 50 ml and 5 ml were used for polarography. Start tension was -0.075 V, and peak tension -0.20 V. Calibration was by standard addition to the final solution. [P.O.Ka.]

**821 - Polarographic characteristics of antimony in supporting electrolytes containing EDTA** (in Japanese). T. Yoshino (Faculty of Engineering, Yamaguchi University, Ube-shi, Yamaguchi, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1012-1019.

In the experiments, the unbuffered supporting electrolytes ( $\mu = 0.3-0.7$ ) of EDTA (2.5-100 *mM*) were used in the absence of gelatin at a concentration of 1 *mM* Sb<sup>3+</sup>.

The single waves (probably for reduction occurring in two stages) were observed at pH 4-5 and 7-8 in media containing 10-100 *mM* and 100 *mM* EDTA, respectively. Distinct two-step reduction waves were observed at pH 5.6-7 and 9-10 in media containing 2.5-100 *mM* and 10-100 *mM* EDTA, respectively. The  $E_{1/2}$  values of Sb<sup>3+</sup> waves in these media were found to be -0.55 to -0.8 V vs. S.C.E. at pH 3-10.

The Sb<sup>3+</sup> waves were controlled by diffusion in acidic and neutral media containing 2.5-100 *mM* EDTA and were controlled by the rate of reaction in the alkaline media containing 100 *mM* EDTA. For the analysis of Sb<sup>3+</sup>, it is recommended that the pH values of the media should be adjusted to between 4-5, and more than 10 times as much EDTA as Sb<sup>3+</sup>, in molar ratio, should be added.

In supporting electrolyte containing 10 *mM* EDTA and 0.001% gelatin at pH 4.6, the  $E_{1/2}$  values of Sb<sup>3+</sup> were constant (about -0.7 V vs. S.C.E.) and the value of the diffusion current constant was 1.64 ± 0.04. [Ta.Fu.]

**822 - Polarographic determination of oxygen in nitrogen** (in German). W. Heimann and K. Wissler (Institut für Lebensmittelchemie der Technischen Hochschule, Karlsruhe, Deutschland). *Z. anal. Chem.*, 185 (1962) 266-273.

The oxygen content of nitrogen is determined by bubbling the gas through distilled water (containing traces of gelatin) for 10 min. The oxygen content of the solution is then followed polarographically.

Determination of oxygen in very small volumes of gases is carried out as follows: The supporting electrolyte (0.05% KCl and 0.01% gelatin) is saturated with air and is transferred into the polarographic vessel, which is closed with a piston to keep the air over the solution. After the determina-

tion of the current at  $-0.6$  V vs. S.C.E. the gas to be measured is added to the air under the piston. After shaking the gas with the solution for 2-3 min, the current is read again at the same electric tension. The difference between the two values is a measure of the oxygen content in the nitrogen, taking into consideration Henry's law. The relation between the difference, and the concentration of oxygen in nitrogen, is quadratic. [E.Pun.]

**823 - Polarographic determination of small amounts of selenium** (in German). R. Bock and H. Kau (Institute of Inorganic and Nuclear Chemistry, University of Mainz, Germany). *Z. anal. Chem.*, 188 (1962) 28-39.

Es wurde festgestellt, dass Se in der Na-K-Tartrat-Grundlösung oder in Li-Citrat-Grundlösung gut zu bestimmen ist. In beiden Fällen ändert sich mit dem pH die Diffusionskonstante. Die Stufe ist proportional mit der Se-Konzentration im Gebiete von  $0-15$   $\mu\text{g/ml}$ .

Im Konzentrationsbereich von  $10-15$   $\mu\text{g/ml}$  wird besser eine basische Grundlösung ( $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ ) benützt. Die Halbstufenspannung beträgt in saurem Medium  $-0.6$  (GKE) V aber in alkalischem Medium einen Wert von etwa  $-1.4$  bis  $-1.6$  (GKE) V. Es wurde eine Reihe von Grundlösungen überprüft, diese zeigten aber keine besondere Vorteile den erwähnten Grundlösungen gegenüber. Die oszillopolarographische Arbeitsweise bietet keine Vorteile im Vergleich der normalen Polarographie. [E.Pun.]

**824 - The polarographic behaviour of the molybdenum heteropolyacids** (in German). K. Grasshoff and H. Hahn (Chemical Institute, University of Würzburg, Würzburg, Germany). *Z. anal. Chem.*, 180 (1961) 18-31.

The authors describe the polarographic behaviour of the molybdenum-germanium heteropolyacids. Three, more or less clear, steps are recognizable in the polarographic reduction. Acetic acid, sodium acetate, sodium chloride and sodium citrate are suitable for the molybdenum-germanium acids' determination. The formation constant of the molybdenum-germanium acid is  $1.6 \cdot 10^{-11}$ . The method for this polarographic reduction is also suitable for determining small amounts of germanium. [Di.Ciò.]

**825 - Determination of uranium in plutonium metal, Pu compounds and nitric or hydrochloric solutions of Pu** (in English). U.K.A.E.A. Products Group, Windscale, Cumberland, Great Britain). *Nuclear Sci. Abstr.*, 16 (1962) 807, Abstract No. 6367.

**826 - Polarographic determination of uranium and molybdenum in the presence of each other** (in English). G. S. Deshmukh and J. P. Srivastava (Chemistry Laboratory, Banaras Hindu University, Varanasi, India). *Z. anal. Chem.*, 176 (1960) 28-34.

Molybdenum and other elements which are reducible to unstable lower valence states generally interfere in the determination of small quantities of uranium. Since polarographic reduction offers the advantage of speed in operation, some techniques have been found and described for the simultaneous determination of the two metals in the presence of hydrazine sulphate. [Di.Ciò.]

**827 - Polarographic analysis. II. Polarography of uranium in sulphate solutions** (in English). I. M. Issa, R. M. Issa and L. A. Shalaby (National Research Centre, Cairo, and Assiut University, Egypt, U.A.R.). *Z. anal. Chem.*, 176 (1960) 250-256.

The authors describe the polarographic determination of uranium(VI) in  $\text{H}_2\text{SO}_4$  solutions of different concentrations, and also in solutions containing  $\text{Na}_2\text{SO}_4$ . In very dilute sulphuric acid solutions ( $0.01$  M), the polarogram consists of three waves of almost equal heights, each corresponding to the uptake of one electron. The second and third waves combine when the  $\text{H}_2\text{SO}_4$  concentration is increased to  $0.055$  M, or by adding  $\text{Na}_2\text{SO}_4$  or sulphosalicylic acid. In  $0.25$  M  $\text{H}_2\text{SO}_4$ , or in the presence of EDTA, the second wave shifts to a less negative electric tension. The diffusion current measured at  $-0.6$  V is proportional to the U(VI) concentration in  $0.25-0.6$  M  $\text{H}_2\text{SO}_4$ . This is not the case in the presence of EDTA. [Di.Ciò.]

**828 - Polarographic analysis. III. Polarographic behaviour of uranium in phosphoric acid solutions** (in English). I. M. Issa, R. M. Issa and L. A. Shalaby (National Research Centre, Cairo, and Assiut University, Egypt, U.A.R.). *Z. anal. Chem.*, 176 (1960) 257-263.

In phosphoric acid solution containing gelatin as supporting electrolyte a single wave is obtained, corresponding to the reduction of U(VI) to U(IV). In the absence of gelatin the wave is often characterised by maxima that can be suppressed by this maximum suppressor, especially when the concentration of  $\text{H}_3\text{PO}_4$  is  $> 1$  M. The half-wave electric tension shifts to less negative values on increasing the phosphoric acid concentration, so that in  $10$  M  $\text{H}_3\text{PO}_4$  solution, reduction starts at zero applied electric tension.

The diffusion coefficient of the phosphate complex varies with the concentration of  $\text{H}_3\text{PO}_4$ , in the presence or absence of gelatin. [Di.Ciò.]



**829 – Polarographic studies of some carboxylate and chloracetate pentammine cobalt(III) complexes** (in Japanese). T. Yanagi and K. Kuroda (Department of Chemistry, Kyoto Gakugei University, Fushimi-ku, Kyoto, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1641–1644.

Some carboxylate and chloracetate-pentammine cobalt(III) nitrates,  $(\text{CoRCO}_2(\text{NH}_3)_5)(\text{NO}_3)_2$ , ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3$ ), were studied polarographically in 0.1 *M* KCl and 0.25 *M*  $\text{K}_2\text{SO}_4$  solution with a dropping mercury electrode. All of these complexes were reduced irreversibly in two steps at the dropping mercury electrode: the first wave corresponded to the reduction  $\text{Co(III)} \rightarrow \text{Co(II)}$ , and the second to  $\text{Co(II)} \rightarrow \text{Co(0)}$ . Each wave height was proportional to the concentration of the complexes in the range of  $5 \cdot 10^{-4} - 5 \cdot 10^{-3}$  *M*. The half-wave electric tension of the second wave for each complex was found to be almost the same, while that of the first wave was different. Negative values increased in the following order:  $\text{CH}_3\text{CO}_2^- > \text{CH}_2\text{ClCO}_2^- > \text{CHCl}_2\text{CO}_2^- > \text{CCl}_3\text{CO}_2^-$ ;  $n\text{-C}_3\text{H}_7\text{CO}_2^- > \text{C}_2\text{H}_5\text{CO}_2^-$ ,  $\text{CH}_3\text{CO}_2^- > \text{HCO}_2^-$ . This result might indicate that the polarographic stability of  $(\text{CoRCO}_2(\text{NH}_3)_5)^{2+}$  decreases as the basicity of the ligands  $\text{RCO}_2$  decreases. No quantitative relation was found between the shift of half-wave electric tension and the basicity. [Ta.Fu.]

**830 – Amperometric vanadimetric determination of cobalt with two polarized electrodes** (in English). Asha Varma (Banaras Hindu University, Varanasi, India). *J. Sci. Ind. Research (India)*, 21 B (1962) 142–144.

Amperometric vanadimetric determination of bivalent cobalt with two polarized electrodes at 100mV. was carried out in the presence of 0.5% EDTA in 0.05 *N*  $\text{H}_2\text{SO}_4$  medium. EDTA combined more firmly with cobalt(III) than with cobalt (II), and lowered the redox electric tension to a point where cobalt became titratable with vanadate ion. The results are accurate up to  $10^{-4}$  *M*. At still lower concentrations the end-point is sharp and reproducible, the maximum error being  $\pm 5.0\%$ . [R.S.Sa.]

**831 – Effect of the nature and concentration of the supporting electrolyte on the half-wave potential and diffusion current. II** (in English). S. N. Mukherjee and Mrs. A. Chakravarti (Jadavpur University, Calcutta, India). *J. Indian Chem. Soc.*, 39 (1962) 149–154.

The diffusion current and half-wave electric tensions were measured at different concentrations of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions in the presence of different concentrations of the supporting electrolytes KCl,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$  and  $\text{CaCl}_2$ . Both these parameters exhibit variations which could not be accounted for by changes in viscosity alone. An attempt was made to explain the observations in the light of the influence of: (1) ionic strength, (2) interionic forces, and (3) the hydrogen overvoltage. [R.S.Sa.]

**832 – Amperometric, iodometric determination of nickel(II) at constant voltage with two polarised electrodes** (in English). D. Singh and A. Varma (Electrochemical Laboratory, Banaras Hindu University, Varanasi, India). *Z. anal. Chem.*, 188 (1962) 6–10.

This dead-stop method is based on the fact that slightly soluble  $\text{Ni(II)}$  dimethylglyoxime is oxidisable to  $\text{Ni(IV)}$  dimethylglyoxime (which is also slightly soluble) with iodine at pH 6.5 in ammoniacal solution. The oxidation reaction is quantitative. Between the two dead-stop electrodes an overvoltage of only 30 mV must be applied, because the electrode reaction of  $\text{I}_3/\text{I}_2$  is nearly reversible. The oxidation electric tension of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  is 1.78 V and of  $\text{I}_3$  to  $\text{I}_2$  is 0.53 V, but the oxidation electric tension of the Ni system is lowered by complex formation with dimethylglyoxime in such a way, that the oxidation of nickel with iodine will be possible. Determination of nickel is possible at concentrations of approximately  $10^{-4}$  *M* with a fair degree of accuracy. [E.Pun.]

**833 – Polarographic and oscillographic determination of nickel** (in German). D. Weiss (Institut für Erzforschung, Prag, Tschechoslowakei). *Z. anal. Chem.*, 185 (1962) 273–286.

Nickel, in a base solution containing 0.1 *M*  $\text{NH}_4\text{SCN}$ , 0.4 *M* urotropin and 0.5 *M*  $\text{NH}_4\text{ClO}_4$  (or  $\text{NH}_4\text{Cl}$ ) gives a polarographic wave at  $-0.70$  V vs. S.C.E., having the characteristics of a two-electron reduction. In order to eliminate the disturbing effect of  $\text{Fe(III)}$ , it is reduced with sulphite in acidic medium before the addition of the base solution to be determined. The traces of  $\text{Fe(III)}$  are complexed with salicylic acid, and then the sample is freed from oxygen. Cu, Pb and Tl react at an electric tension more positive than Ni, therefore large amounts of this element cause disturbing effects. The Cd wave coincides, and disturbs the measurements. Cr, Ti, V and Mo have the same effect. Urotropin precipitates Cr and Ti, but, as the surface of the precipitate adsorbs Ni, the authors use tiron as complex-forming agent, which eliminates (with the exception of Cr) the disturbing effect. Using tiron, the complexes of hydrolyzable metals (Sb, Bi, U(VI), In(III) and Sn(IV)) cause similar interference.

In the above mentioned base solution (in the absence of gelatin), the sensitivity of the oscillo-

polarographic break lies at  $10^{-6} M$ . Thus, the direct determination of Ni in metallic Al, Mn, Ti, Ce and In is possible in the presence of iron. [E.Pun.]

**834 - Nicotinamidoxime as an analytical reagent. III. Polarographic studies on the nature of the nickel complex and spectrophotometric determination of the metal** (in English). K. K. Tripathi and D. Banerjee (Department of Inorganic and Analytical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India). *Z. anal. Chem.*, 176 (1960) 91-96.

In alkaline medium, nicotinamidoxime is first oxidized, possibly to an azo type compound, which interacts with nickel(II) forming a deep blue coloured compound. This was demonstrated by means of polarographic investigations. At pH 10.5-11.5, in the presence of an excess of the amidoxime, the colour develops almost instantaneously and is stable for at least 24 h. The system follows Beer's law in the range 0.3-10 p.p.m. of Ni, and the optimum range for measurement is 3-10 p.p.m. Of the common anions, only  $CN^-$  and EDTA interfere; interference of  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Al^{3+}$ ,  $Ti^{4+}$ ,  $Zr^{4+}$  and  $Th^{4+}$  may be masked by excess tartrate. [Di.Ciò.]

**835 - The use of polarography in organic chemistry** (in Hungarian). P. Zuman (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Magyar Kém. Lapja*, 17 (1962) 8-11.

After a short and general introduction, applications of the polarographic method for analytical, preparative and structure-determining purposes are discussed. (28 references.) [J.Inc.]

**836 - Polarography in formate media** (in English). G. S. Deshmukh (Banaras Hindu University, Varanasi, India). *J. Sci. Ind. Research (India)*, 21 B (1962) 144.

The use of sodium formate in place of KCNS as supporting electrolyte for the polarographic estimation of cations has been suggested. The preferential choice of formate is due to the absence of any wave of its own and the development of well-defined polarograms, with  $E_{1/2}$  almost identical to that obtained in the presence of thiocyanate under comparable operating conditions. [R.S.Sa.]

**837 - Oscillopolarographic investigations of some alkoxy silanes** (in Hungarian). T. Damokos (Institute of Inorganic Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 175-178.

The  $dE/dt = f(E)$  curves of tetraethoxysilanes, methyl- and phenyl-ethoxysilanes, obtained by oscillopolarographic methods, show a characteristic incision at  $Q$  values of 0.50-0.60. The constancy of the  $Q$  value at the incision depends on the molecular weight of the compound under test. The depth of incision — all parameters being constant — is roughly proportional to the number of ethoxy groups in the molecule. The parallelism between specific oscillopolarographic activities and dipole moments indicates a connection between activity and molecular structure. [J.Inc.]

**838 - Quantitative polarographic determination of aliphatic esters** (in English). T. Österhd and M. Prytz (Yrkeshygienisk Institut, Blindern, Oslo, Norway). *Acta Chem. Scand.*, 15 (1961) 1923-1926.

Reaction mixtures of pure aliphatic esters with hydroxylamine were polarographed at well defined concentrations in ethanol-water solutions of tetrabutyl ammonium iodide, buffered with tetraethyl ammonium hydroxide. The height of the resulting hydroxamic acid curves shows a proportionality with the original concentration of ester. [G.Ekl.]

**839 - Polarographic studies in sarkomycin. VI. The behaviour of sarkomycin S<sub>1</sub> and S<sub>2</sub> in alkaline solution** (in English). Keiji Ida (Meiji Seika Kaisha Ltd., Tokyo, Japan). *Agr. Biol. Chem. Japan*, 25 (1961) 643-651.

Sarkomycin S<sub>1</sub>, which is the di-(2-carboxy-5-oxocyclopentyl)disulphide, and sarkomycin S<sub>2</sub>, which is the corresponding monosulphide, both give three waves when polarographed at the dropping mercury electrode. The plot of the half-wave electric tension vs. pH shows an inflection in passing to alkaline conditions. [Gio.Ser.]

**840 - Polarographic studies on sarkomycin. VII. Polarographic estimation of sarkomycin by treatment with sodium sulphite** (in English). Keiji Ida (Meiji Seika Kaisha Ltd., Tokyo, Japan). *Agr. Biol. Chem. Japan*, 25 (1961) 652-654.

An indirect method of determination of sarkomycin is described. This is based on the disappearance of the polarographic waves of sarkomycin at the dropping mercury electrode when  $Na_2SO_3$  is added. The difference in the currents before and after the addition is proportional to the sarkomycin concentration. The method can be applied to pharmaceutical preparations, where the direct method is not applicable because of the impurities. [Gio.Ser.]

**841 – Polarographic studies on sarkomycin. VIII. Amperometric titration with potassium bromate using the rotating platinum electrode** (in English). Keiji Ida (Meiji Seika Kaisha Ltd., Tokyo, Japan). *Agr. Biol. Chem. Japan*, 25 (1961) 655–657.

Sarkomycin A (2-methylene-3-oxocyclopentane-1-carboxylic acid) can be determined by following its bromination amperometrically with bromate–bromide. The impurities which are generally present in preparations do not interfere, since they are not brominated. [Gio.Ser.]

**842 – Investigation of the reduction of nitrobenzene-3-sulphonic acid on a dropping mercury electrode** (in Hungarian). F. Péter and I. Szabados (Institute of Practical Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 145–149.

Die Reduktion der Nitrobenzol-3-sulphonsäure wurde an tropfender Quecksilberelektrode in Britton–Robinson-Pufferlösung, im pH-Bereich 2–12, in verschiedenen Konzentrationen ( $10^{-3}$ ,  $10^{-4}$  und  $5 \cdot 10^{-5}$  M) bei verschiedenen Quecksilberniveaus und Temperaturen untersucht. Aus den Ergebnissen wurde festgestellt, dass die Reduktion weder in alkalischem noch in saurem Medium die Bildung des Hydroxylaminderivates überschreitet. In saurem Medium entsteht gleichzeitig eine Adsorptionsnachstufe. [J.Inc.]

**843 – Polarographic and oscillopolarographic determination of the semicarbazones of vanillin and ethylvanillin. IV** (in German). S. Woggon. *Ernährungsforschung*, 6 (1961) 331–337.

The polarographic determination of the semicarbazones of vanillin and ethylvanillin is easier than that of the original compounds because of the higher diffusion coefficients. The effects of pH, temperature and semicarbazone concentrations have been studied, by the normal and oscillographic techniques. [Gio.Ser.]

**844 – Polarographic study of photoisomerisation of o-nitrobenzaldehyde** (in English). C. B. Roy (R. P. M. College, Hoogly, India). *J. Indian Chem. Soc.*, 38 (1961) 955–958.

Kinetics of the photochemical reaction of o-nitrobenzaldehyde was studied polarographically in the range of 4360–3130 Å. The aldehyde was reduced at the dropping Hg electrode and a C–V curve with a well-defined diffusion range is obtained. The investigation further reveals that polarographic methods of analysis, with a suitable electro-reducible substance, may be employed to determine the total quantity of light that causes a photochemical reaction. Hence a polarograph may be used as an actinometer. [R.S.Sa.]

**845 – Polarographic activity of dihydro- $\alpha$ -pinene-3-thiol.** *Chem. pr ůmysl*, 11 (1961) 518–520.

Dihydro- $\alpha$ -pinene-3-thiol, in concentrations of  $5 \cdot 10^{-4}$  to  $5 \cdot 10^{-3}$  M was dissolved in 50 ml of ethanol–cyclohexanol (4 : 1) mixture. After addition of 25 ml of 1 M LiOH the solution was diluted to 100 ml with water. After deaeration, an aliquot was used for polarographic determination between –0.4 and –1.1 V. [Gio.Ser.]

**846 – The determination of aldrin in fertiliser** (in English). H. N. Wilson and M. Phillipson (Imperial Chemical Industries Ltd., Billingham Division, P.O. Box No. 6, Billingham, Co. Durham, Great Britain). *Analyst*, 87 (1962) 441–443.

1 g of sample was extracted in a small column-type extraction tube, sealed at the bottom by filter paper discs, with ca. 25 ml of warm 10% nitric acid saturated with aldrin. The remaining sample was washed with distilled water until free of Cl<sup>-</sup>, and dried at 100° for five min. The sample was transferred on the filter paper discs to a combustion flask, which was filled with oxygen and contained 20 ml of 5-volume H<sub>2</sub>O<sub>2</sub>. It was burnt using a filter paper wick. The flask was shaken vigorously for 15 min, and the solution was transferred quantitatively to a titration cell, 5 ml conc. HNO<sub>3</sub> were added and the solution was diluted to 150 ml with water. The Cl<sup>-</sup> from the aldrin was titrated with 0.01 N AgNO<sub>3</sub> using a dead-stop end-point, according to Price and Coe (*Analyst*, 84 (1959) 55). The method gave results very close to a previously used extraction method which took about 6 hours. [P.O.Ka.]

**847 – Investigation of adsorption phenomena occurring at the dropping mercury electrode.**

**I. The effect of sulphuric acid ester derivatives of leuco anthraquinone on the reduction of nitrobenzene-3-sulphonic acid in acidic media** (in Hungarian). F. Péter, I. Szabados and Gy. Pályi (Institute of Practical Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 101–105.

The effect of a sulphuric acid ester derivative of anthraquinone (Indigosol yellow V) on the polarographic reduction wave of nitrobenzene-3-sulphonic acid in Britton–Robinson buffer solution of pH 3.3 was investigated. It was found that this surface-active compound splits the reduction wave of the nitro group into two parts. The contribution of the height of the wave, which moves towards negative electric tensions in the sum of the limiting currents, increased with increasing concentra-

tion of the surface-active compound. At sufficiently high concentrations, the whole wave moved towards more negative electric tensions. The effect of mercury level and temperature on the wave height were also investigated. The observed phenomena may be used for quantitative determination of Indigosol yellow V, or similar compounds. [J.Inc.]

**848 – Polarographic and voltammetric determination of purines and pyrimidines. Analysis of mixtures** (in English). D. L. Smith and P. J. Elving (Michigan University, Ann Arbor, Mich., U.S.A.). *Nuclear Sci. Abstr.*, 16 (1962) 808, *Abstract No.* 6370.

**849 – Polarographic determination of ascorbic acid in wine** (in German). W. Diemair, J. Koch and D. Hess (Univ.-Institut für Lebensmittelchemie, Frankfurt a.M., and Institut für Obst- und Gemüseverwertung, Geisenheim/Rhg., Germany). *Z. anal. Chem.*, 178 (1961) 330-334.

A method is given for the polarographic determination of ascorbic acid in wine with particular regard to the influence of oxygen and ethyl alcohol. [Di.Ciò.]

**850 – Polarographic determination of the purity of commercial bilirubin** (in Czechoslovakian). B. Tvaroha (Pathological Laboratory, Charles University, Prague, Czechoslovakia). *Časopis lékáru českých*, 100 (1961) 869-871.

Bilirubin yields one anodic wave and two cathodic waves in alkaline solution. In 0.1 N NaOH all the waves are well defined, and can be used for the determination of bilirubin. The second cathodic wave, which has a half-wave electric tension of  $-1.48$  V, is particularly suitable, and was used in this work. The results obtained are compared with those obtained by colorimetry of a solution of standard bilirubin in  $\text{CHCl}_3$  at  $450 \mu\mu$ . [Gio.Ser.]

**851 – The quantitative determination of amino acids as copper complex** (in Japanese). M. Matsuoka (Osaka Works, Tanabe Pharmaceutical Co., Higashiyodogawa-ku, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1032-1036.

The polarographic determination of amino acids as the copper complex has already been proposed by Jones and Martin. This method is based on the fact that a soluble copper-amino acid complex is formed on addition of a copper phosphate suspension to an amino acid solution. However, errors are encountered in this method. This may be attributed to a relatively high solubility of copper phosphate, because the reaction used takes place between a liquid and a solid. Therefore, a better method was devised in which a liquid-liquid reaction is employed. In this method, a solution of a copper salt, instead of a copper phosphate suspension, is added to the sample solution. The pH is adjusted to 9.0, the precipitated  $\text{Cu}(\text{OH})_2$  is filtered off, and the remaining cupric ion in the filtrate is determined polarographically. [Ta.Fu.]

**852 – Determination of amino acids by oxidation with potassium periodate** (in Japanese). M. Matsuoka (Osaka Works, Tanabe Pharmaceutical Co., Higashiyodogawa-ku, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1193-1197.

Potassium periodate is reduced to potassium iodate when it oxidizes threonine, serine, methionine, cystine or cysteine. Therefore, polarographic determination of these amino acids was attempted by measuring the difference in the wave heights of  $\text{IO}_4^-$  ion before and after the oxidation of the amino acids.

It was found that potassium periodate reacts with threonine or serine at a quantitative ratio of 1 : 1 at pH 9, with cystine at a 2 : 1 ratio, and with cysteine at a 3 : 2 ratio at pH 7, and with methionine at a 1 : 1 ratio at pH 4. Other amino acids do not interfere in this method. The recommended procedure for determining the amino acids is described, and the effect of other oxidizing substances was investigated. [Ta.Fu.]

**853 – Determination of amino acids by oxidation with cerium(IV)** (in Japanese). M. Matsuoka (Osaka Works, Tanabe Pharmaceutical Co., Higashiyodogawa-ku, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1198-1202.

Ce(IV) is reduced to Ce(III) when it oxidizes tryptophan, tyrosine or methionine. In the present paper, the polarographic determination of the above amino acids was investigated by measuring the difference in the wave heights of Ce(IV) before and after the oxidation of the amino acids.

It was found that, in 0.5 M  $\text{H}_2\text{SO}_4$  solution, Ce(IV) reacts with tryptophan at a quantitative ratio of 10 : 1 at  $20^\circ$ , with tyrosine at a 5 : 1 ratio at  $20^\circ$  and with methionine at a 10 : 1 ratio at  $100^\circ$ . Phenylalanine does not interfere in this method at  $20^\circ$ . Methionine sulfone does not interfere, even at  $100^\circ$ . Cystine and cysteine interfere, but other amino acids do not. Recommended procedures for the analysis of the mixture of amino acids were described, and the effects of the interfering substances were also examined. [Ta.Fu.]

**854 – Comparison of colorimetric, iodometric and polarographic methods for the determination of peroxide number** (in German). G. Janicek, J. Pokorny and V. Pliska (College of Chemical Technology, Prague, Czechoslovakia). *Nahrung*, 5 (1961) 399–410.

The changes of peroxide content in sunflower seed-oil during autoxidation were followed. Colorimetry of fat peroxides with  $TiCl_4$  is satisfactory and sensitive. The use of three methods allows a distinction to be made between two main groups of peroxides: reactive peroxides can be determined by the colorimetric and polarographic methods, while unreactive peroxides can only be determined by the iodometric method. The reactive peroxides are formed almost exclusively at room temperature. Increasing the temperature and time decreases the ratio between reactive and unreactive peroxides. This ratio is a maximum when the peroxide formation is also at a maximum.

[Gio.Ser.]

See also abstracts nos. 780, 781, 782, 791, 858, 933.

#### 4. Potentiometry

**855 – Ultramicro analytical methods. I. Laboratory equipment and methods** (in German). W. Helbig (Zentralinstitut für Kernphysik, Rossendorf, Rossendorf über Dresden, Deutschland). *Z. anal. Chem.*, 182 (1961) 15–19.

Laboratory equipment for ultramicro analytical methods and for potentiometry and amperometry is described.

[Di.Ciò.]

**856 – Differential electrolytic potentiometry. VI. The precision and accuracy of applications to acid–base titrations with antimony electrodes** (in English). E. Bishop and G. D. Short (Washington Singer Laboratories, The University, Exeter, Great Britain). *Analyst*, 87 (1962) 467–477.

If a small stable current is passed between two antimony electrodes immersed in an aqueous solution, the pH at the anode will be slightly lower, and that at the cathode slightly higher, than in the bulk solution because of generation of  $H^+$  at the anode and of  $OH^-$  at the cathode. The concomitant electrode tension changes mean that there is a difference of tension between the two electrodes equivalent to that produced by the addition of a small increment of titrant at the mid-point of the increment, *i.e.* an instantaneous measure of  $\Delta E/\Delta V$  at the operating point. Hence, the curve showing the relation between the tension difference and volume of titrant is closely similar to the first derivative of the tensiometric curve, the end-point being shown as a peak. Titrations of the four combinations of strong and weak acids and bases showed that this technique gave results of high precision and excellent accuracy for all except weak acid–weak base titrations.

[P.O.Ka.]

**857 – A rapid method of forecasting the end-point in potentiometric titrations** (in English). J. F. Herringshaw (Chemistry Department, Imperial College of Science and Technology, London, Great Britain). *Analyst*, 87 (1962) 463–466.

In order to save the time involved in plotting a complete titration curve and obtaining the point at which  $dE/dV$  is a maximum, a method of successive approximation is suggested, based on the relations (I) and (II), for redox and precipitation titrations, respectively:

$$\frac{i}{i} = 4^{0n} \frac{\Delta E}{\Delta V} - \frac{i}{\frac{1}{2}(V_1 + V_2)} \quad (I)$$

$$\frac{i}{i} = 4^{0z} \frac{\Delta E}{\Delta V} - \frac{i}{\frac{1}{2}(V_1 + V_2)} \quad (II)$$

where  $V_1$  and  $V_2$  are two volumes of titrant,  $\Delta V = (V_2 - V_1)$  and  $\Delta E$  is the change of indicator electrode tensions between  $V_1$  and  $V_2$ ;  $n$  and  $z$  are the number of electrons involved, or the valency of the anion whose concentration is indicated by the indicator electrode; and  $i$  is then the estimated volume required to be added to  $\frac{1}{2}(V_1 + V_2)$  for the end-point.

[P.O.Ka.]

**858 – Electrochemistry in anhydrous ethylenediamine. Effects on salts and solvent in potentiometry and polarography** (in English). W. B. Scheep, R. E. Bayer, J. R. Siefker,

J. Y. Kim, P. W. Brewster and F. C. Schmicht (Indiana University, Bloomington, Ind., U.S.A.). *Nuclear Sci. Abstr.*, 16 (1962) 668, *Abstract No.* 5268.

**859 – Potentiometric studies of the titration of weak acids with tetrabutylammonium hydroxide** (in English). L. W. Marple, J. S. Fritz (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.). *Anal. Chem.*, 34 (1962) 796.

A special comparison electrode for the titration with tetrabutylammonium hydroxide in *tert.*-butyl alcohol, pyridine, and acetone is described. The system of the comparison electrode is S.C.E./aqueous phase–Me<sub>4</sub>NCl–H<sub>2</sub>O–organic/organic phase–Me<sub>4</sub>NCl–H<sub>2</sub>O–organic. The sources of amine, carbonate and silver impurities in the titrant were determined and techniques for their removal evaluated. The stability of the base in several solvents was studied. A glass indicating electrode was used. The results of several titrations are given. The titrations are reproducible to within 2–5 mV. [Kl.Gr.]

**860 – Recent advances in non-aqueous titrimetry by instrumental methods. III. Potentiometric titrations** (in English). J. T. Stock and W. G. Purdy (Department of Chemistry, University of Connecticut, Storrs, Conn., U.S.A.). *Lab. Practice*, 11 (1962) 191–193.

The authors examine the numerous recent publications concerning non-aqueous titrimetry. Potentiometry is the most used instrumental technique. This is due to the ready availability of electronic pH meters designed to operate with a glass electrode, that is a good acid–base indicator in many solvents. Other electrodes are equally, or more, suitable, especially in strongly basic solvents. [Di.Ciò.]

**861 – Recent advances in non-aqueous titrimetry by instrumental methods. IV. The antimony–antimony oxide and other electrodes** (in English). J. T. Stock and W. G. Purdy (Department of Chemistry, University of Connecticut, Storrs, Conn., U.S.A.). *Lab. Practice*, 11 (1962) 290–293.

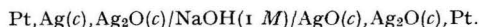
The authors examine many new publications about the antimony–antimony oxide electrode, the micro antimony “absorption electrode”, platinum, silver and many miscellaneous indicator electrodes. [Di.Ciò.]

**862 – Potentiometric titration in non-aqueous cerimetry** (in English). G. P. Rao and A. R. V. Murthy (Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 12, India). *Z. anal. Chem.*, 182 (1961) 358–366.

A method for potentiometric determination of potassium iodide and hydroquinone in non-aqueous media, using ammonium nitrate–ammonium cerate as oxidant, is described. A platinum indicator electrode and a glass or antimony comparison electrode were used. The direct potentiometric titration of xanthate with ammonium nitrate–ammonium cerate in non-aqueous media yields low values in the presence of a platinum indicator electrode. [Di.Ciò.]

**863 – A study of the silver(I) oxide–silver(II) oxide electrode** (in English). J. F. Bank and A. B. Garrett (McPherson Chemical Laboratories, Ohio State University, Columbus, Ohio, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 612–615.

For studying the Ag<sub>2</sub>O–AgO electrode the following cell was used:



At 25° the E.M.F. found for this cell was  $0.2623 \pm 0.0002$  V; the standard free energy change for the cell reaction was  $-6049 \pm 5$  cal, the entropy change was  $5.07 \pm 0.02$  cal/deg. and the enthalpy change was  $-4537 \pm 11$  cal; Knowing the oxidation potential of the Ag–Ag<sub>2</sub>O electrode at 25°, it was possible to calculate the standard oxidation potential of the Ag<sub>2</sub>O–AgO electrode at 25°. This potential appeared to be highly dependent on the method of preparing AgO samples. In the case of AgO prepared by alkaline oxidation of Ag<sub>2</sub>O by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, the oxidation potential of the couple Ag<sub>2</sub>O–AgO was found to be  $-0.604$  V. From the preceding values and from existing thermodynamic data, the free energy and enthalpy of formation, and entropy of AgO at 25° were determined to be, respectively, 3463 cal,  $-2769$  cal and 1381 cal/deg. [H.Hur.]

**864 – Potentiometric titration of silver with thioglycolic acid** (in Japanese). Yukio Takeuchi (Wako Pure Chemical Industries Ltd., Higashi-ku, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1644–1647.

To establish a simple and rapid determination for silver in Cu–Ag alloy, the use of thioglycolic acid standard solution was re-examined (*cf. ibid.*, 82 (1961) 859). Silver, when titrated with standard thioglycolic acid solution shows no visually detectable end-point, but the end-point becomes unam-



biguous in the potentiometric titration as it can be read from an abrupt change in the electric tension between platinum and calomel electrodes.

In this titration the voltage jumps twice. It is well known that  $\text{AgSCH}_2\text{COOAg}$  is formed at the first jump, and  $(\text{AgSCH}_2\text{COOH})_2\text{AgSCH}_2\text{COOAg}$  is formed at the second.

If the first point is taken for the end-point, there will be no interference due to copper(II), and therefore silver in the Cu-Ag alloy may be determined easily and rapidly. With this method  $10^{-1}$ – $10^{-4}$  M silver may be determined. [Ta.Fu.]

**865 – Indirect potentiometric determination of zinc, silver, indium and halogens with hydroquinone** (in German). J. Blažek, J. Doležal and J. Zýka (Institut für analytische Chemie der Karlsuniversität, Prag, Tschechoslowakei). *Z. anal. Chem.*, 180 (1961) 241–246.

An indirect potentiometric method for determination of a heavy-metal is described, by adding a solution containing ferricyanide ions. The solution is titrated with hydroquinone. The method gives good results for Zn, Ag, In, Cl, Br, hypochlorite, hypobromite and bromate determination, even in the presence of one extraneous ion. No results were obtained for the determination of Ni, Co, Mn, Cu, Cd, Pb, Mo, U. [Di.Ciò.]

**866 – Back titration with mercuric nitrate in alkaline medium. Analysis of tertiary mixtures of Hg(II) with some other metals** (in English). H. Khalifa and F. A. Osman (Microanalytical Department of the National Research Centre, Dokki, Egypt, U.A.R.). *Z. anal. Chem.*, 178 (1960) 116–123.

The analysis of tertiary mixtures each containing mercury(II) is described. The procedure involves combining the method of back titration with mercuric nitrate in alkaline medium and the volumetric methods, which make use of masking agents, such as cyanide. The mercury(II) content in the mixtures is determined potentiometrically with KI, using silver amalgam as the indicator electrode. [Di.Ciò.]

**867 – Estimation of lanthanum by hexacyanoferrate(II)** (in English). J. N. Gaur (Department of Chemistry, University of Rajasthan, Jaipur, India). *Z. anal. Chem.*, 185 (1962) 357–361.

The composition of lanthanum hexacyanoferrate(II) complex was examined by gravimetric, potentiometric and conductometric measurements. Conductometric curves are invalid for evaluation. Potentiometric titration curves also cannot be clearly interpreted. From the three types of measurement the composition of the precipitate was established to be  $\text{LaKFe}(\text{CN})_6$ . [E.Pun.]

**868 – Oxidation of trivalent cerium with potassium permanganate in alkaline solution** (in English). I. M. Ossa and M. G. E. Allam (Chemistry Department, Cairo and Assiut University, Egypt, U.A.R.). *Z. anal. Chem.*, 182 (1961) 244–251.

The oxidation of trivalent cerium with permanganate is described under a variety of conditions, including reduction of permanganate with trivalent cerium, both in the presence and absence of telluric acid. Good results are obtained in the presence of this acid, provided that the alkalinity of the reaction medium is not less than 1 N, in order to overcome the effect of acid present in the cerous solution. The concentration of cerium(IV) was determined potentiometrically, using a standard ferrous ammonium sulphate solution. [Di.Ciò.]

**869 – Potentiometric titration of cerium with thioglycolic acid** (in Japanese). Yukio Takeuchi (Wako Pure Chemical Industries Ltd., Higashi-ku, Osaka, Japan). *J. Chem. Soc. Japan Pure Chem. Sect.*, 82 (1961) 1647–1649.

Ce(IV) reacts with thioglycolic acid in a low pH range. The mole ratio of Ce(IV) to thioglycolic acid was found to be 2 : 1. Volumetric titration of Ce(IV) was unsuccessful, as the end-point of this reaction was visually undetectable, but Ce(IV) was determined easily and rapidly using potentiometric titration.

Fe(III), Cu(II), Cd(II), Ni(II), Pb(II), etc. do not interfere in this method. [Ta.Fu.]

**870 – Electrometric studies on the precipitation of hydrous oxides of some quadrivalent cations. II. Precipitation of thorium hydroxide from solutions of thorium salts** (in English). R. P. Singh and N. R. Banerjee (University of Delhi, India). *J. Indian Chem. Soc.*, 39 (1962) 255–259.

Precipitation of thorium hydroxide from thorium sulphate, chloride and nitrate solutions by sodium hydroxide was studied by means of continuous conductometric and pH titrations. It is shown that when equilibria are attained, the precipitates consist of basic salts having the compositions  $\text{Th}(\text{OH})_{3.14}(\text{SO}_4)_{0.43}$ ,  $\text{Th}(\text{OH})_{3.12}\text{Cl}_{0.88}$  and  $\text{Th}(\text{OH})_{3.7}(\text{NO}_3)_{0.3}$ . The anion penetration is practically of the same order in the cases of sulphate and chloride, but in the case of nitrate it is much less. Using baryta for thorium sulphate solutions, it has been found that, although a basic salt of about

the same composition is precipitated initially, it gives up its sulphate ions on addition of more baryta, leaving behind almost pure thorium hydrous oxide. [R.S.Sa.]

**871 – Determination of the ammoniacal nitrogen in fertilizers by titration with sodium hypochlorite** (in German). Z. Rezac and M. Figarovà (Forschungsinstitut für anorganische Chemie, Ústí nad Labem, Czechoslovakia). *Z. anal. Chem.*, 176 (1960) 115-118.

A method is described for determining ammoniacal nitrogen in fertilizers by titration with sodium hypochlorite solution. Phosphate Calgon S is added to prevent precipitation. The end-point is determined by the dead-stop method. [Di.Ciò.]

**872 – Studies in condensed phosphates. V. Reaction of sodium metaphosphate with ferric salt in solution** (in English). R. C. Mehrotra and V. S. Gupta (University of Gorakhpur, India). *J. Indian Chem. Soc.*, 39 (1962) 97-102.

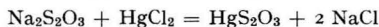
Conductometric and potentiometric titrations of ferric chloride with sodium metaphosphate solution indicated a sharp inflection point at the molar ratio of  $\text{FeCl}_3 : 1/n(\text{NaPO}_3)_n$  at 1:1.5, corresponding to the formation of a solid precipitate having the composition  $\text{Fe}_2(\text{OH})_3(\text{PO}_3)_3$ . Comparative reactions of orthophosphate have also been investigated. [R.S.Sa.]

**873 – Potentiometric investigation of the dissociation constant of substituted dithiophosphoric acid** (in German). H. Bode and W. Arnswald (Anorganisch-chemisches Institut der Technischen Hochschule, Hannover, Deutschland). *Z. anal. Chem.*, 185 (1962) 99-110.

Contradictions in the literature of the dissociation constant of diethyldithiophosphoric acid were solved by the authors. By potentiometric titrations and pH measurements this substance was found to be a strong acid. [E.Pun.]

**874 – Mercurimetric determination of thiosulphate** (in German). S. A. Kiss (Borsodi Veggi Kombinát, Kazincbarcika, Hungary). *Z. anal. Chem.*, 182 (1961) 251-253.

A new potentiometric method for thiosulphate determination is described. Mercury(II) chloride may react with thiosulphate according to the following reaction:



Potential jumps of 220-360-300 mV may be measured at pH 4.5-6.5-10.0, respectively. [Di.Ciò.]

**875 – Back titration with mercuric nitrate in alkaline medium. Estimation of small amounts of Cr(III) and analysis of its binary mixtures with some other metals** (in English). H. Khalifa and M. M. Khater (Faculty of Science, Cairo University, Giza, Egypt, U.A.R.). *Z. anal. Chem.*, 178 (1960) 260-265.

The authors describe a rapid, reliable and accurate method for the determination of Cr(III) (from 50  $\mu\text{g}$  to 15 mg), based on back titrating excess EDTA solutions in the presence of chromium versenate with mercuric nitrate in alkaline media. [Di.Ciò.]

**876 – The potentiometric determination of chlorides in tobacco** (in English). R. A. Nelson (Internal Revenue Service, Washington 25, D.C., U.S.A.). *J. Assoc. Offic. Agr. Chemists*, 43 (1960) 518.

The potentiometric determination of chlorides in tobacco with  $\text{AgNO}_3$  (Ag, and Ag-AgCl electrodes) is described. The results (0.1-3.5% Cl) are compared with those obtained with gravimetric analysis. The reproducibility is good and the potentiometric method very rapid. [Di.Ciò.]

**877 – Amperometric titration with the help of selenites. Determination of cobalt** (in English). G. S. Deshmukh, V. D. Assand and A. Joseph (Chemistry Laboratory, Banaras Hindu University, Varanasi 5, India). *Z. anal. Chem.*, 182 (1961) 324-329.

Recent studies of the application of amperometry to the determination of cobalt as tellurite and tungstate, have made possible a new procedure for rapid amperometric titration of Co, based on precipitation of cobalt as selenite. The use of 50% overall concentration of methanol is essential for these titrations, which were performed at an applied electric tension of -1.5 V v.s. S.C.E. The procedure gives good results, which agree well with the formula  $\text{CoSeO}_3$  for cobalt selenite. [Di.Ciò.]

**878 – Ultramicro analytical methods. II. Amperometric microdetermination of plutonium** (in German). W. Helbig (Zentralinstitut für Kernphysik, Rossendorf, Rossendorf über Dresden, Deutschland). *Z. anal. Chem.*, 182 (1961) 19-24.

An amperometric method for the microdetermination of plutonium is described, in the range of 50-100  $\mu\text{g}$ . (See also abstract no. 855.) [Di.Ciò.]

**879 – Ultramicro analytical methods. III. Potentiometric microdetermination of plutonium**



(in German). W. Helbig (Zentralinstitut für Kernphysik, Rossendorf, Rossendorf über Dresden, Deutschland). *Z. anal. Chem.*, 182 (1961) 84-88.

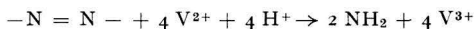
A potentiometric method for the microdetermination of plutonium is described. 0.1  $\mu\text{g}$  plutonium can be determined. The plutonium is reduced to  $\text{Pu}^{3+}$  with a  $\text{Cr}^{2+}$  solution, and then titrated with  $\text{Ce}^{4+}$ . [Di.Ciò.]

**880 - The use of potassium manganate in quantitative analysis. VI. Determination of formic acid and analysis of formic, oxalic and acetic acid mixtures** (in German). M. L. Polak (Laboratorium für analytische Chemie der Universität, Amsterdam, Die Niederlande). *Z. anal. Chem.*, 176 (1960) 34-38.

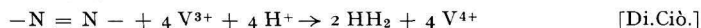
The formic acid is quantitatively oxidised in 1 hour at 60° by potassium manganate. The excess manganate used in the oxidation is titrated potentiometrically with a 0.02 *M* arsenite solution. [Di.Ciò.]

**881 - Direct reductometric titration of azo dyes with vanadium(II) sulphate** (in Czechoslovakian). M. Matrka and Z. Sagner (Forschungsinstitut für organische Synthesen Pardubice-Rybitvi, C.S.S.R.). *Chem. průmysl*, 10 (1960) 474-475.

The direct reductometric titration of azo dyes, e.g. methyl orange and methyl red, with vanadium (II) sulphate is described. The reactant consumption is lower than the theoretical equilibrium value:



This is caused by the following equilibrium:



**882 - Ascorbimetric determination of a thioazine and thioazone** (in German). E. Ruzicka and M. Kotoucek (Chemisches Institut der Naturwissenschaftlichen Fakultät der Universität, Olomouc, Lidicka, Czechoslovakia). *Z. anal. Chem.*, 180 (1961) 429-433.

Ascorbic acid reduces thioazine and thioazone to colourless leuco compounds. The reaction is quantitative at 60-70°, and in a 2 *N* HCl or  $\text{H}_2\text{SO}_4$  solution. The determination is carried out potentiometrically with a platinum and a calomel electrode. Amines, nitrocompounds, phenols and sulphur compounds do not interfere. [Di.Ciò.]

**883 - Acid-base properties of solochrome violet R.S.** (in English). H. Khalifa and S. W. Bishara (National Research Centre, Dokki, Cairo, Egypt, U.A.R.). *Z. anal. Chem.*, 178 (1960) 184-193.

Solochrome violet R.S. proved to be a suitable indicator in titrating some mineral and organic acids as well as a colorimetric reagent for the microdetermination of vanadium. The dye's acid-base properties have been studied, and the *pK* values (4.35, 7.4 and 9.45, corresponding to the three steps of ionisation) can be evaluated from pH values obtained during the potentiometric titration of the free acid with a free base. [Di.Ciò.]

See also abstracts nos. 769, 777, 781, 789, 790.

## 5. Conductometry

**884 - Recent advances in non-aqueous titrimetry by instrumental methods. I. Conductometric and high-frequency titrimetry** (in English). J. T. Stock and W. G. Purdy (Department of Chemistry, University of Connecticut, Storrs, Conn., U.S.A.). *Lab. Practice*, 11 (1962) 21-24.

The authors examine 300 new publications which appeared during the past two years on non-aqueous titrimetry, concerned with conductometric and high-frequency techniques. (See also abstracts nos. 860 and 861.) [Di.Ciò.]

**885 - High frequency titration by the method of heterodyne beats** (in Russian). V. M. Gorokhovskii, Yu. Yu. Samitov and N.V. Tremasov. *Izvest. Vysshikh. Ucheb. Zavedenii, Khim. i. Khim. Tekhnol.*, 3 (1960) 805-809.

A new method of high frequency titration is described. The high frequency used for the titration is in phase with a constant frequency from another generator. By this method, titrations can be carried out in a very short time with an error not higher than 5% for strong acids in concentrations lower than  $10^{-4}$  N. The method is suitable for determining  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and total hardness in waters of low salt content, such as petroleum waters. [Gio.Ser.]

**886 – Measurement of ion mobility in sodium iodide solutions by means of radioactive isotopes** (in Hungarian). E. Inzelt and S. Lengyel (Institute of Physical Chemistry, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 151–156. Es wurde eine Methode zur Bestimmung der Ionenbeweglichkeiten mit Hilfe von radioaktiven Isotopen ausgearbeitet, mittels welcher die Beweglichkeiten und Überführungszahlen der Ionen selbst in höchst konzentrierten Lösungen bestimmt werden können. Setzt man radioaktive Isotope in die Lösung, die in einem langen Rohr sich befindet und misst man während der Elektrolyse die Aktivitätsveränderung in bestimmten Stellen des Rohres entlang, so kann man aus den Messungsergebnissen die Beweglichkeiten der Ionen berechnen. Mit Hilfe der Methode wurden die Ionenbeweglichkeiten in Natriumjodid-Lösungen, im Konzentrationsgebiet 0.1 bis 8.76 Mol/l gemessen. Die Summe der gemessenen Ionenbeweglichkeiten stimmte mit den entsprechenden äquivalenten Leitfähigkeitswerten der Literatur bei jeder Konzentration überein. Die Werte der Überführungszahlen wurden auch ermittelt. [J.Inc.]

**887 – Electrical conductance of solutions of salts in liquid metals. Potassium iodide in potassium** (in English). H. R. Bronstein, A. S. Dworkin and M. A. Bredig (Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *J. Chem. Phys.*, 34 (1961) 1843–1844.

The solubility of halides  $\text{KX}$  in liquid potassium is very high, attaining complete miscibility in all proportions. This paper reports previous measurements of electrical conductivity in salt-rich KI-K solutions. Conductivity increases with increasing metal content. The measurements were made up to  $700^\circ$ .

Between mole fractions  $N_{\text{KI}} = 0$  and 0.20, the data can be expressed (in  $\mu\Omega/\text{cm}$ ) by:

$$\rho = aN_{\text{KI}} + b$$

where:  $a = 920 \mu\text{ohmcm}$  and  $b = 58 \mu\text{ohmcm}$ . The increase was interpreted as being caused by gradual establishment of metallic conduction. [G.Mar.]

**888 – Transport numbers in pure fused salts. The alkali metal chlorides** (in English). F. R. Duke and A. L. Bowman (Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 626–627.

A radiochlorine tracer technique was used to determine the transport number of the chlorine ion in fused alkali chloride salts. The movements of the ions through a fine porosity membrane were measured using constant current electrolysis. The values obtained are compared with predictions of other workers. It may be concluded that transport numbers of these salts do not correspond to any simple function of the mass or radius of the ions. [H.Hur.]

**889 – Conductometric titration of barium with potassium tellurite** (in English). S. Prasad and B. L. Khandelwal (Banaras Hindu University, Varanasi, India). *J. Indian Chem. Soc.*, 39 (1962) 84–88.

Conductometric titrations between barium chloride and potassium tellurite at several concentrations in aqueous and alcoholic media were carried out. Direct as well as inverse titrations were shown to be possible over a wide range of barium concentrations. In the presence of 40–50% over all concentration of ethanol, the results were found to be quantitative and the break in titration curves was more marked and accurate. The formation of normal barium tellurite is suggested, at a molar ratio of Ba to Te of 1:1. [R.S.Sa.]

**890 – Studies on arsenites of rare-metals. VII. Composition of thorium arsenites by conductometric methods** (in English). R. S. Saxena and G. P. Saxena (Government College, Kota, Rajasthan, India). *J. Sci. Ind. Research (India)*, 21B (1962) 145–146.

The formation and composition of thorium arsenites, obtained by the interaction of  $\text{Th}(\text{NO}_3)_4$  and  $\text{NaAsO}_2$  at pH 9.85, 11.25 and 12.28 were investigated by conductometric titration at various concentrations of the reactants. In each case a well-defined break in the titration curves was obtained at a point corresponding to the formation of different compounds, depending upon the pH of the medium:  $\text{ThO}_2 \cdot 2 \text{As}_2\text{O}_3$  at pH 9.85;  $\text{ThO}_2 \cdot \text{As}_2\text{O}_3$  at pH 11.25 and  $3 \text{ThO}_2 \cdot 2 \text{As}_2\text{O}_3$  at pH 12.28. The composition of thorium arsenites, which can be expressed by the general formula,  $X\text{ThO}_2 \cdot 2\text{As}_2\text{O}_3$ , depends upon the H ion concentration of alkali arsenites. [R.S.Sa.]

**891 – Electrometric study on polymolybdates of rare metals. Composition of thorium molybdates as a function of the pH** (in English). R. S. Saxena and M. L. Mital (Government College, Kota, Rajasthan, India). *J. Sci. Ind. Research (India)*, 21B (1962) 92–93.

The course of reactions between  $\text{Th}(\text{NO}_3)_4$  and different alkali molybdates was followed by means of conductometric titrations at different pH ranges, in aqueous and aqueous-alcoholic media. Distinct breaks in titration curves were obtained at points corresponding to the formation of normal thorium molybdate:  $\text{ThO}_2 \cdot 2\text{MoO}_3$  in the pH range 4.2–5.6, and thorium paramolybdate  $\text{ThO}_2 \cdot 4.66\text{MoO}_3$  at pH 3.0–3.7. Conductometric study does not suggest the formation of di-, tri- and meta-molybdates of thorium. [R.S.Sa.]

**892 – Conductometric estimation of thorium in dilute thorium chloride** (in English). P. G. Menon and D. Singh (Department of Chemistry, Banaras Hindu University, Varanasi, India). *Z. anal. Chem.*, 176 (1960) 264–269.

The results of thorium chloride conductometric titrations with oxalic acid, ammonium oxalate and silver nitrate, are given. The titrations were carried out at high dilutions (0.001, 0.0005 and 0.00033 M) of the chloride, and the best results were obtained with oxalic acid as titrant. For mixtures of thorium and cerous chlorides only the equivalence point corresponding to the complete precipitation of both thorium and cerium is indicated. [Di.Ciò.]

**893 – Spectrophotometric and conductometric study of the reaction between vanadyl sulphate and Rochelle salt** (in English). P. K. Bhattacharya, M. C. Saxena and S. N. Banerjee (University of Saugar, Saugar, India). *J. Indian Chem. Soc.*, 39 (1962) 240–242.

Spectrophotometric and conductometric studies of the reaction between vanadyl sulphate and Rochelle salt indicate that a coloured complex of composition 1 : 1 is formed. The system obeys Beer's law. The dissociation constant of the complex was found to be  $5.62 \cdot 10^{-6}$ . [R.S.Sa.]

**894 – Controlling the purity of heavy water by conductivity** (in Italian). L. Selmi (C.I.S.E., Milan, Italy). *Nuclear Sci. Abstr.*, 16 (1962) 810, *Abstract No.* 6392.

**895 – Determination of macro amounts of fluoride by steam distillation and high frequency titration** (in English). R. C. Calkins (Metals Division Res., Kaiser Aluminium and Chemical Corporation, Permanente, Calif., U.S.A.). *Anal. Chem.*, 34 (1962) 837.

The fluoride to be determined, especially in the presence of large amounts of aluminium, was steam distilled. Optimum conditions for the distillation procedure were studied. The fluoride was titrated in the distillate with lanthanum acetate. The end-point was indicated by the high frequency titration technique. 1–10 mg fluoride from the distillate were pipetted into the titration vessel and made up to about 110 ml with water. The pH was adjusted to 4.5. 1 ml acetate buffer was added (0.2 N acetic acid and 0.2 N sodium acetate) and the titration was carried out in 0.4 ml increments with  $\sim 0.018$  N lanthanum acetate. The fluoride was determined from a standard curve. Standard deviation is below 0.4%. [Kl.Gr.]

**896 – The determination of hydrolysis constants of oximes of aromatic carbonyl compounds by conductometry** (in Japanese). K. Arai (Chemistry Laboratory, College of General Education, Osaka University, Toyonaka-shi, Osaka, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1434–1436.

Hydrolysis constants of oximes of substituted benzaldehydes were successfully determined by conductometry, and their logarithms were found to be proportional to Hammett's  $\sigma$  values, except for nitro derivatives. The proportionality is similar to that observed in the addition compounds of benzaldehyde with sodium bisulfite or with hydrogen cyanide. [Ta.Fu.]

**897 – A study of the polymerisation of thermosetting polymers by electrical resistivity techniques** (in English). R. W. Warfield and M. C. Petree (U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Md., U.S.A.). *SPE Trans.*, 1 (1961) 1–6.

Es wird die isotherme Polymerisation einer Reihe von Epoxy-, Polyester- und Polyurethan-Polymeren nach einer Widerstandsmessmethode untersucht. Die Widerstandsmessung erfolgt dabei mit Gleichstrom und einer die Probe aufnehmenden Zelle mit konzentrischen Elektroden und Teflonisolation. Die Auswertung wird mit Widerstand-Zeit-Diagrammen und der Polymerisations-temperatur als Parameter vorgenommen. Zusätzlich aufgestellte Diagramme mit dem Widerstand als Ordinate und der reziproken absoluten Temperatur als Abszisse ergeben für die verschiedenen Polymerisationsprozesse Geraden, aus deren Steigung (nach der Arrhenius Gleichung) die Aktivierungsenergie berechnet werden kann. Die Methode wird zur Bestimmung der Polymerisationsgeschwindigkeit und des Polymerisationsgrades empfohlen und lässt Einblicke über eine bei der Polymerisation auftretenden Kettenverzweigung erwarten. [Fr.Oe.]

See also abstracts nos. 768, 774, 775, 788, 855, 867, 870, 872, 934.

## 6. Electrolysis

**898 – Analytical applications of the mercury electrode** (in English). J. A. Page, J. A. Maxwell and R. P. Graham (Department of Chemistry, University of Toronto, Toronto (first author); Geological Survey of Canada, Ottawa (second author); Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada (third author)). *Analyst*, 87 (1962) 245-272.

This is a review article, with 423 references, covering the following topics involving electrolysis with significant concentration changes, thus excluding polarography and chronopotentiometry. (1), Reductions without external control of electrode tension; (2), reductions and oxidations with external control of electrode tension; (3), coulometric determinations at controlled current; (4), amalgamometry. The period covered by the review is 1948-1960. [P.O.Ka.]

**899 – Electrodeposition of molybdenum** (in English). T. T. Campbell (U.S. Bureau of Mines, Albany, Oreg., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 119-123.

The electrodeposition of molybdenum from various non-aqueous solvents was studied. Thin films of Mo, or alloys of Mo with Fe, Pt or Pb were obtained. It was shown that Mo halides form a wide variety of complex compounds with the solvents used. Solubility data for a number of Mo compounds in organic solvents are given. [H.Hur.]

**900 – Electrolytic reduction of organic compounds** (in English). F. D. Popp and H. P. Schultz (Department of Chemistry, University of Miami, Fla., U.S.A.). *Chem. Revs.*, 62 (1962) 19-40.

A review of the electrochemical reduction of organic compounds covering the literature on the subject since 1940. For the sake of completeness, reference is made to papers published prior to 1940. The discussion includes general principles, a survey of the factors that influence electro-organic reductions and a general review of the methods and apparatus used. Electro reductions of different types of organic compounds are considered. Polarographic reduction is not discussed. 386 references. [Su.Mo.Ce.]

**901 – Electrophoresis of serum proteins** (in German). R. Bieth (Institute of Chemical Biology, Faculty of Medicine, The University, Strasburg, France). *Röntgen-Lab. Praxis*, 13 (1960) L 141-L 143.

The author describes the different separation methods for proteins groups, based upon electrophoresis. [Di.Ciò.]

## 7. Coulometry

**902 – Controlled potential coulometry in fused lithium chloride-potassium chloride eutectic** (in English). J. D. van Norman (Brookhaven National Laboratory, Upton, N.Y., U.S.A.). *Anal. Chem.*, 34 (1962) 594.

Coulometry at controlled electric tension was adapted to analysis in fused salts. A bismuth pool electrode was used for the deposition of Zn and Cd, and a platinum gauze electrode for Ni. The method was also applied to determine uranium in uranium-bismuth alloys. Apparatus and solvent purification are described in detail. After a vacuum pretreatment the metals were deposited in the eutectic melt at a temperature of 450°. Zn, Cd, and U were then determined by anodic stripping of the deposited metals. The analyses were made with an accuracy of  $\pm 1\%$  for each component. A platinum wire was taken as the anode with respect to the cathode during the stripping procedure. [Kl.Gr.]

See also abstracts nos. 781, 786, 787, 801, 898, 923.

## 8. Electrophoresis

**903 – Countercurrent electrophoresis on paper. VI. Electrophoretic distribution isotherms** (in English). Z. Fidler, J. Vacik, J. Dvorak and O. Grubner (Department of Physical

Chemistry, Charles University, Prague, Czechoslovakia). *J. Chromatog.*, 7 (1962) 228-241. Assumptions concerning the similarity of paper chromatography and paper electrophoresis, as regards the nature of the substances analysed with the immobile phase, were verified. Glueckauf's method for constructing distribution isotherms from chromatographic measurements was applied to electrophoretic measurements. It was proved that the isotherms obtained in this way are identical with the isotherms obtained by the direct method, when the dependence of the mobility in free solution on the concentration can be neglected.

The values of  $R_F$ , the electrophoretic mobility in free solution  $U_0$  and the velocity  $u_0$  obtained both by direct measurement and by calculation were proved to be identical. [Authors]

**904 - High voltage paper electrophoresis instrument** (in German). H. Hofferek, W. Pawlitschek and H. Wolfgang (Institut für Phytopathologie, Aschersleben, Germany). *Pharmazie*, 15 (1960) 308-309.

A new high voltage paper electrophoresis instrument is described for separating 8 amino acids (in acetic acid buffer solution, pH 2, 150 min electrolysis) or asparagine and glutamine mixtures (acetic acid-triethylamine buffer solution, pH 3.5, 30 min electrolysis) with 1000 V (2.5-3 mA). [Di.Ciò.]

**905 - Identification of the chemical form of radioactive ions at submicromolar concentrations** (in English). R. W. Henkens and D. R. Kalkwarf (Hanford Laboratories Operation, General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 34 (1962) 830.

Paper electrophoresis is used to separate radioactive ions without sample concentration. The free solution mobilities are calculated from their apparent mobilities in the paper. The chemical forms of the ions are determined by comparing the migrations with those of known ions under identical conditions. [Kl.Gr.]

**906 - Paper chromatographic and paper ionophoretic separation of platinum and gold group metals** (in German). E. Blasius and M. Fischer (Anorganisch-Chemisches Institut der technischen Universität, Berlin, Deutschland). *Z. anal. Chem.*, 178 (1960) 28-33.

It is possible to separate Pd, Pt, Au, Se and Te by means of paper ionophoresis with a buffer solution (1 N HCl and  $\text{CH}_3\text{COONa}$ ). The applied electric tension is 110-130 V and the ionophoresis time 1-2 h. [Di.Ciò.]

**907 - Continuous electrophoretic separations of radioactive rare earth mixtures. II. Separation of  $^{147}\text{Nd}$ ,  $^{169}\text{Er}$ ,  $^{177}\text{Lu}$ ;  $^{144}\text{Ce}$ ,  $^{153}\text{Gd}$ ,  $^{177}\text{Lu}$ ; and  $^{144}\text{Ce}$ ,  $^{147}\text{Pm}$ ,  $^{160}\text{Tb}$ ,  $^{169}\text{Er}$ ,  $^{177}\text{Lu}$  in 0.05 M lactic acid** (in English). Z. Konrad-Jakovac and Z. Pučar (Institute "Rudjer Bošković", Zagreb, Yugoslavia). *J. Chromatog.*, 7 (1962) 380-384.

Radioautographs of the continuous electrophoretic separations of the rare earth mixtures  $^{147}\text{Nd}$ ,  $^{169}\text{Er}$ ,  $^{177}\text{Lu}$ ;  $^{144}\text{Ce}$ ,  $^{153}\text{Gd}$ ,  $^{177}\text{Lu}$ ; and  $^{144}\text{Ce}$ ,  $^{147}\text{Pm}$ ,  $^{160}\text{Tb}$ ,  $^{169}\text{Er}$ ,  $^{177}\text{Lu}$  in 0.05 M lactic acid are given. After each radioautograph the activities of the separated rare earths, which correspond to a 0.5 hour run, are given diagrammatically. Radioautographs of the two-dimensional electrochromatographic separations of the two three-component mixtures are also given. The separation of the five-component mixture required an enlargement of the basic apparatus in the horizontal direction, and appropriate modifications of the apparatus. [Authors]

**908 - Zone electrophoresis in ethyl alcohol buffer solution** (in English). J. Porath and K. Storiko (Biochemisches Institut der Universität Uppsala, Schweden). *J. Chromatog.*, 7 (1962) 385-391.

Aniline dyes can be efficiently separated by column electrophoresis in ethanolic buffer solutions; the apparatus used is described. From the electrophoretic behaviour of the organic substances investigated, conclusions concerning their intramolecular interactions may be derived. [Authors]

**909 - Paper electrophoretic determination of 5-hydroxy tryptophane, 5-hydroxytryptamine and 5-hydroxy indolacetic acid** (in German). A. Carcasona, F. Unterharnscheidt, J. Cervos-Navarro and W. Geller (Institut für Neuropathologie der Universität, Bonn, Deutschland). *Klin. Wochschr.*, 38 (1960) 457-460

The paper-electrophoretic determination of the three indol derivatives is carried out at 3.5 V/cm, 1 mA,  $10^2$ , and at pH 5.05, 7.00 and 8.6, respectively. [Di.Ciò.]

**910 - Zone electrophoresis of crude pituitary extract** (in English). J. A. Tuyman, H. G. Kwa and H. Bloemendal (Department of Experimental Biology and Department of Biochemistry, Netherlands Cancer Institute, Amsterdam, The Netherlands). *J. Chromatog.*, 7 (1962) 39-44.

Starch block electrophoresis, under standardized conditions, of water-soluble protein hormones

from rat anterior pituitary tissue is described. The recovery of four of the five hormones assayed proved to be 90-100%. A pure growth-promoting substance has been isolated by a single run. The maxima of the separated hormone activities do not coincide with the protein peaks, with the exception of somatotrophic hormone (STH). Follicle stimulating hormone (FSH), thyroid stimulating hormone (TSH) and interstitial cell stimulating hormone (ICSH) were partially separated. The peaks of both FSH and TSH contained only one major contaminant (ICSH). [Authors]

**911 - Starch gel electrophoresis of wheat-gluten proteins with concentrated urea** (in English). J. H. Woychik, J. A. Boundy and R. J. Dimler (Northern Regional Research Laboratory, Peoria, Ill., U.S.A.) *Arch. Biochem. Biophys.*, 94 (1961) 477-482.

A new technique is applied to the separation of components of wheat gluten. The electrophoresis is conducted in aluminium lactate buffer pH 3.1 containing 3 M urea. Starch gel at a concentration of 18% is used as stabilising medium. The use of urea allows the separation of four new components from gluten; eight new components are displayed in gliadin, and a water-soluble fraction obtained from gluten shows the presence of at least nine protein components. [Gio.Ser.]

**912 - Method of scanning paper electrophoresis strips and its application to the study of plasma proteins** (in English). C. A. Broomfield, and H. A. Scheraga (Department of Chemistry, Cornell University, Ithaca, N.Y., U.S.A.). *J. Biol. Chem.*, 236 (1961) 1960-1967.

A new method is described for the detection of proteins on an electrophoresis strip. The method is based on the fact that if an electrode is connected to a wet paper strip and a second electrode is drawn along the strip, an electric tension is generated when the second electrode comes in contact with a protein band. This effect is enhanced if metal ions are bonded to the proteins and the scanning electrode is made of the same metal. In this way different patterns are obtained with the same plasma using different metals. The method may be used to detect more selectively certain components of protein mixtures. [Gio.Ser.]

**913 - Interaction of non-ionic detergents with protein in paper electrophoresis** (in English). R. M. Dowben, W. R. Koehler and G. Barrieux (Department of Medicine, Northwestern University, Chicago, Ill., U.S.A.). *Clin. Chem.*, 7 (1961) 482-487.

The effect of detergents on paper electrophoresis of serum proteins and of some crystalline proteins was studied. At low concentrations a more rapid migration and sharper peaks were obtained, due to a decreased affinity of proteins for paper. At higher concentrations slower migration and broader peaks result from the formation of complexes between the proteins and the detergent. On glass fibre paper, which has a lower affinity for proteins, only the latter effect is displayed. Non-protein material has a higher migration rate due to the first effect. [Gio.Ser.]

**914 - The separation of nucleotides from acid-soluble tissue extracts by high-voltage paper electrophoresis** (in English). H. M. Klouwen (Radiological Institute of the Organization for Health Research, T.N.O., Rijswijk, Z.H., The Netherlands). *J. Chromatog.*, 7 (1962) 216-222.

A method is presented for the analysis of nucleotides present in acid-soluble extracts from animal tissues. The method is based on the principle of high-voltage electrophoresis and consists of applying this method to acid-soluble extracts isolated from animal tissues. The nucleotide pool is separated into 12-13 fractions; the contents and purity of these fractions are further investigated.

[Author]

**915 - Rapid quantitative paper electrophoretic technique for determining A<sub>2</sub>-haemoglobin** (in English). T. Johnson and O'N. Barret (Walter Reed Army Medical Center, Washington, D.C., U.S.A.). *J. Lab. Clin. Med.*, 57 (1961) 961-965.

The sample was dissolved, to a suitable concentration (ca. 7%), in 50% glycerol and applied to a paper strip. The electrophoresis was carried out in barbital buffer of  $\mu$  0.037 and pH 9.1 for 3 h at 350 V. The dried strip was stained with bromophenol blue and examined using a densitometer with an automatic integrator. [Gio.Ser.]

**916 - Size of sample in starch electrophoresis of cellulase** (in English). G. L. Miller and R. Birzgalis (Pioneering Research Division, Quartermaster Research and Engineering Center, Natick, Mass., U.S.A.). *J. Chromatog.*, 7 (1962) 33-38.

Amounts of cellulase varying over a 100-fold range (0.02-20 mg) gave comparable patterns when subjected to starch electrophoresis. Resolution of components appeared to be better, however, with small than with large sized test samples. Evidence was also obtained which suggested that dissociable complexes occur in the enzyme. [Authors]

See also abstracts nos. 784, 785.



## 9. Other methods

**917 – Preparation of carrier-free radioactive atomic products by electrochromatographic methods using an anodic polarised platinum powder column** (in Hungarian). I. Mádi (Institute of Physical Chemistry, Kossuth University, Debrecen, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 129–137.

Unter Anwendung von asymmetrischer Elektrodensysteme wurde der zeitliche Verlauf der elektrolytischen Abscheidung verschiedener radioaktiver Ionenarten ( $Ce^{144}$ ,  $Pr^{144}$ ,  $Y^{90}$ ,  $Yb^{175}$ ) auf der Platinanode untersucht. Aus den Messungen wurde festgestellt, dass aus den Oxydprodukten der einzelnen Ionenarten höchstens je eine monomolekulare Oberflächenschicht an der Anode zustande kommen kann. Es wurde ferner gefunden, dass sich die Logarithmen der Zahlenwerte der Verteilungskoeffiziente und der mit der Isothermenmethode bestimmten Aktivstellen der Platinoberfläche mit den pH-Werten linear ändern. Auf Grund der Untersuchungsergebnisse wurde zur Trennung trägerfreier radioaktiver Atomarten ein mit Elektrolyse verbundenes, chromatographisches Verfahren ausgearbeitet. Es wurden die Chromatogramme einiger mit Hilfe von anodisch polarisierter Platinpulverkolonne durchgeführten Trennungsversuche mitgeteilt. Z.B. Die Trennung von  $Sr^{90}$ ,  $Y^{90}$ ,  $Pr^{144}$ ,  $Ce^{144}$  wurde mit Hilfe von verdünnten Salpetersäure-Lösungen als Eluiermitteln, bei einer Spannung von 3 V durchgeführt. [J.Inc.]

**918 – The influence of the self-damping of coaxial leads in measuring liquids with low dielectric losses** (in German). H. Wirth (Institut zur Entwicklung chem. phys. Analysemethoden, Weilheim/Obb, Deutschland). *Mitt. Inst. Entwickl. chem. phys. Analysemethoden, Weilheim/Obb.*, 3 (1961) 57–63.

Bei der Messung hoher dielektrischer Verluste spielt die Eigendämpfung einer koaxialen Messleitung keine Rolle. Dagegen muss bei sehr kleinen Verlusten der Eigenverlust der Messleitung berücksichtigt werden. Die Eigenwelligkeit der Leitung wird aus der Halbwertsbreite der Spannungs-Maxima und Minima berechnet. Die anzubringende Korrekturfunktion ist bei dem Dezidekameter DK 08 in guter Näherung eine Gerade. Der Betrag der Korrektur hängt von der Stellung des Kurzschlusschiebers in der Leitung ab. [Fr.Oe.]

**919 – Chronopotentiometry with saw impulses** (in German). H. Hoffmann and W. Jaenicke (Institut für physikalische Chemie der technischen Hochschule, Karlsruhe, Deutschland). *Z. anal. Chem.*, 186 (1962) 93–102.

Die Chronopotentiometrie mit Rechteckimpuls ermöglicht nicht immer ein gut auswertbares Ergebnis. Mit gleicher Transitionszeit gibt der sägezahnförmige Stromimpuls bessere Resultate als der Rechteckimpuls. Der Zusammenhang zwischen Transitionszeit und Konzentration wird durch die folgende Gleichung beschrieben:

$$\beta\tau^{3/2} = \frac{3zF\sqrt{\pi D}}{4} c$$

wo  $\beta$  die Steigung des Sägezahnimpulses,  $\tau$  die Transitionszeit,  $z$  Elektronenzahl/Formelumsatz,  $F$  Faraday-Zahl,  $D$  Diffusionskoeffizient,  $c$  Konzentration bedeutet.

Die Methode ermöglicht die Anwendung eines größeren Stromes als der Rechteckimpulstechnik und dadurch kann das empfohlene Verfahren zur Bestimmung kürzerer Transitionszeiten und zu reaktionskinetischen Untersuchungen angewendet werden. [E.Pun.]

**920 – Maximum phenomena in the electroanalytical method using potential-step voltammetry** (in Japanese). S. Oka (Shimadzu Seisakusho Ltd., Nakakyo-ku, Kyoto, Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1356–1359.

Effect of suppressing unfavorable maxima of current–electric tension curves in a newly developed method (cf. S. Oka, *ibid.*, 82 (1961) 1202–1206) was studied experimentally, and was compared with the results of conventional polarography. The present method gives current–voltage curves free from the streaming effect of the liquid around the working electrode, which is usually observed in the conventional method with the dropping mercury electrode. Consequently, the maxima of  $Zn^{2+}$  and  $Mn^{2+}$  in 1 N KCl in the conventional method, as well as those of  $Tl^{+}$  and  $Pb^{2+}$  in 1 N  $HNO_3$  and that of  $Ni^{2+}$  in 1 N  $NH_3^{+}$ , 1 N  $NH_4Cl$ , etc. are eliminated, regardless of whether the electrode reaction takes place at the negative or at the positive side of the isoelectric point. With 1 N KCl solution as supporting electrolyte, however,  $Pb^{2+}$  and  $Tl^{+}$  show the maxima, not only in conventional polarography, but also in this method. Furthermore, at the applied voltage at which the maximum current is observed, an anomaly appears on the current–time curve, and an abnormally large current flows through the cell soon after the abrupt change of the electric tension. These phenomena show that the reducible substances (such as  $Tl^{+}$  or  $Pb^{2+}$ ) are concentrated at the electrode surface, and that normal concentration polarization is prevented. Details of the anomaly

on the current-time curve are described, and the behavior of Cl<sup>-</sup> ion co-existing with the reducible substances is also discussed. [Ta.Fu.]

**921 - Determination of uranium in 310 stainless steel ribbon-type final element by the application of the mercury cathode-lead reductor-potassium dichromate method** (in English). R. A. Dunleavy, A. M. Bartruff and M. R. Menke (General Electric Co., Aircraft Nuclear Propulsion Dept., Cincinnati, Ohio, U.S.A.). *Nuclear Sci. Abstr.*, 16 (1962) 667, *Abstract No.* 5263.

**922 - Determination of uranium in 310 stainless steel ribbon-type final element by the application of the mercury cathode-lead reductor-ceric sulphate method** (in English). R. A. Dunleavy, G. L. Contner and J. A. Sweet (General Electric Co., Aircraft Nuclear Propulsion Dept., Cincinnati, Ohio, U.S.A.). *Nuclear Sci. Abstr.*, 16 (1962) 667, *Abstract No.* 5264.

See also abstracts nos. 766, 767, 781, 799, 898.

## 10. Related topics

**923 - Investigation of the electrochemical characteristics of organic compounds. III. Nitroalkanes** (in English). R. Glicksman and C. K. Morehouse (R.C.A. Laboratories, Radio Corporation of America, Princeton, N.J., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 288-294. The electrochemical properties of nitroalkanes were studied by discharging, at constant current, a 0.5 g sample of the nitroalkane cathode material mixed with 0.05 g of Shawinigan acetylene black. For most of the measurements a large volume of an aqueous magnesium bromide electrolyte and a magnesium anode were used. The results were explained on the basis of electron densities in the vicinity of the reducible nitro-group. As indicated from coulometric studies, electrode efficiencies of 36-52% may be obtained. The effect of pH on the operating electric tension was shown to be very small. The performance characteristics of magnesium-nitroalkane dry cells seems to offer some possibilities of practical applications of these compounds in primary cells. [H.Hur.]

**924 - Hydrogen diffusion current on the rotating platinum disc electrode. I. Electrical model of stationary diffusion in the case of a heterogeneous surface** (in Hungarian). F. Nagy and G. Horányi (Central Institute for Chemical Research, Hungarian Academy of Sciences, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 198-201. An electrical analogue was constructed of stationary diffusion with inhomogeneous boundary conditions in a cylindrical tube. The model was an electrolytic cell consisting of a cylindrical Plexiglas tube, having a perforated celluloid membrane in the middle, and platinized platinum electrodes in the two ends. KCl solution was used as electrolyte and the resistance of the cell was measured by a Wheatstone bridge using alternating current. The relation found by the model representation was:

$$R = \frac{1}{\kappa} \left[ 0.240 \left( \frac{1}{r_1} - \frac{1}{r_2} \right) + \frac{l}{r_2^2 \pi} \right]$$

where  $R$  is the resistance of a cylinder of radius  $r_2$ , length  $l$  and specific conductivity  $\kappa$  through which current passes, having a cross section of radii  $r_1$  at one end and  $r_2$  at the other.  $l > 8 r_1$ .

[J.Inc.]

**925 - Hydrogen diffusion current on the rotating platinum disc electrode. II. Determination of the number of active sites** (in Hungarian). F. Nagy, G. Horányi and G. Vértes (Central Institute for Chemical Research, Hungarian Academy of Science, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 202-205.

For de diffusion current  $i$  of hydrogen on a rotating platinum disc electrode, supposing discrete active sites, the following relation was derived as a modification of Levich's equation:

$$\frac{i}{i_c} = \frac{1}{QD} \left[ \frac{1.1 \cdot 10^7}{p} + \frac{1.61 \nu^{1/6} D^{1/3}}{\omega^{1/2}} \right] \frac{1}{c}$$

where  $Q$  is the surface area of the electrode,  $D$  the diffusion constant of hydrogen in solution,  $p$  the density of active sites,  $\nu$  the kinematic viscosity of the solution,  $\omega$  the angular velocity of the electrode and  $c$  the concentration of the hydrogen in the solution. On aged platinized platinum electrodes values of  $1.3 \cdot 10^{10}$  and  $0.6 \cdot 10^{10}$  were found for  $p$ . [J.Inc.]



**926 – The impedance of galvanic cells. IV. Determination of rate constants of rapid electrode reactions from electrode impedance measurements** (in English). M. Lehbach and J. H. Sluyters (Analytical Chemistry Laboratory, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 81 (1962) 301–306.

Rate constants may be determined by plotting the measured cell impedance in the complex impedance plane at varying impedances (*Rec. trav. chim.*, 79 (1960) 1092 and 80 (1961) 469; abstracted *J. Electroanal. Chem.*, 2 (1961) A 155 no. 807, 808). This method will give accurate results only if  $k_{sh} < 10^{-2}$  cm sec<sup>-1</sup>.

The authors suggest a procedure by which values of  $k_{sh}$  up to 0.65 cm sec<sup>-1</sup> may be measured.

First, the cell impedance is plotted in the complex plane for various values of  $*C_{Ox} = *C_{Red}$  at constant frequency. From the coordinates of the centre the value of a parameter  $p = (2\omega)^{1/2}k_{sh}^{-1} (D_{Ox}^{-1/2} + D_{Red}^{-1/2})$  may be found. Through any measured point of this circle and its intersection with the  $Z'$  axis a semicircle can be constructed with its center on the  $Z'$  axis. From the diameter  $q$  of this semicircle and the parameter  $p$  the value of  $\Theta = RT(n^2F^2 *C^2k_{sh})^{-1}$  is obtained.

Limitation of the value of  $k_{sh}$  to about 0.65 cm sec<sup>-1</sup> arises from the fact that, at higher reaction rates, the determination of  $p$  from the first circle cannot be performed with sufficient accuracy.

[C.I.Moo.]

**927 – The effect of sinusoidal current on electrode processes. IX. The decrease of the hydrogen overvoltage on mercury electrodes, caused by alternating current** (in Hungarian). T. Erdey-Gruz, J. Dévay, Gy. Horányi, I. Vajasy and L. Mészáros (Institute of Physical and Chemical Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 143–145.

A model of the decrease of hydrogen overvoltage on mercury electrodes caused by alternating current can be made by connecting in parallel a germanium diode and a capacitance. The tension shifts on the model were found to be in good agreement with those which resulted on the mercury electrode.

[J.Inc.]

**928 – The effect of sinusoidal current on electrode processes. X. The effect of sinusoidal current on hydrogen overvoltage on a platinum cathode** (in Hungarian). T. Erdey-Gruz, J. Dévay and I. Vajasy (Institute of Physical and Chemical Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 185–190.

Die Wirkung von Sinusstrom auf die Wasserstoffüberspannung an einer Platin Kathode wurde mit Hilfe einer selbst konstruierten Einrichtung untersucht. Es wurde gefunden, dass die Wasserstoffüberspannung in  $N$  Schwefelsäure-Lösung durch den auf den polarisierenden Gleichstrom superponierten Wechselstrom herabgesetzt wird. Die Abnahme der Überspannung ist desto grösser, je grösser die Stromdichte und je kleiner die Frequenz des Wechselstromes ist. Die Erscheinung kann dadurch erklärt werden, dass der zeitliche Mittelwert der Überspannung durch die periodischen Schwankungen der Elektrodenspannung wegen der Asymmetrie der Tafel'schen Gleichung verschoben wird. Die gemessenen und die auf Grund dieses Bedenkens berechneten Werte stimmen gut überein.

[J.Inc.]

**929 – The effect of sinusoidal current on electrode processes. XI. The effect of alternating current on the corrosion of the Hg–Zn metal pair** (in Hungarian). T. Erdey-Gruz, J. Dévay and R. Szegedi (Institute of Physical and Chemical Radiology, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 68 (1962) 190–193.

Die Korrosion der Zn-Anode und der vom Galvaneelement Hg–Zn gelieferte Gleichstrom wird in 5% iger KCl-Lösung vergrössert, wenn durch die Elektroden ein Wechselstrom fliesst. Die Zunahme der Korrosion ist desto grösser, je grösser die Intensität und je kleiner die Frequenz des Wechselstromes ist. Der Wechselstrom vergrössert die Korrosion dadurch dass derselbe die Polarisation des Galvaneelementes erniedrigt. Im Falle einer ungleichmässigen Verteilung des Wechselstromes, ist die Korrosion desto grösser, je grösser die Stromdichte des Wechselstromes an der Hg-Elektrode, im Verhältnis zu der Stromdichte an der Zn-Elektrode ist.

[J.Inc.]

**930 – The silver–silver chloride–chlorine solid electrolyte cell** (in English). D. M. Smyth (Sprague Electric Company, North Adams, Mass., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 635–639.

The characteristics of Ag–AgCl–Cl<sub>2</sub> solid electrolyte cells were studied. The cathode was a conducting mixture of KCl<sub>4</sub>, used as a low pressure source of chlorine vapor. The cells, assembled into batteries, delivered currents in the microampere range and had an open-circuit voltage of 1.04 V at 25°, which did not vary more than ±5% over the temperature range +75° to –40°. It was shown that cathode material containing hydrated salts or special greases improve the low temperature properties of the cell. The shelf-life predicted by tarnishing experiments and the shelf-life obtained by extrapolation of accelerated life test at elevated temperatures were both of the order

of decades of years. The aging characteristics showed two stable voltage levels, an initial plateau at 1.05 V and a subsequent plateau at 0.89 V. The internal resistance (of about  $10^5$  ohms) of the cell was controlled, as were the temperature dependence and the current drain, by the ionic conductivity of the AgCl electrolyte. [H.Hur.]

**931 - The oxygen evolution reaction at gold anodes. I. Accuracy of overtension measurements** (in English). S. Barnartt (Research Laboratories, Westinghouse Electric Corporation, Pittsburgh, Penn., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 722-729.

Various sources of error in overtension measurements of the oxygen evolution reaction at gold anodes in 0.1 M  $H_2SO_4$  at 25° are discussed. A new cell design for uniform current distribution is described. At constant current densities, linear oxidation curves corresponding to formation of  $Au_2O_3$  were obtained. These oxidation curves may be interpreted as resulting from a blister mechanism at the oxide-metal interface. The oxide formation rates correspond to current efficiencies too low to have significant depolarizing effects. It was also shown that constant current curves for oxygen evolution exhibit a time effect at low current densities ( $< 3 \cdot 10^{-5}$  A  $cm^{-2}$ ). This behavior is interpreted on the basis of possible simultaneous competing reactions of the oxygen evolution process. Tafel's equation is accurately obeyed for constant current densities in the range  $3 \cdot 10^{-5}$  to  $10^{-2}$  A  $cm^{-2}$ . [H.Hur.]

**932 - Electrodeposition of copper from the sulphamate bath** (in English). S. Venkatachalam (Indian Institute of Science, Bangalore, India). *J. Sci. Ind. Research (India)*, 21D (1962) 145-149.

Plating of copper from sulphamate solutions was investigated. The optimum conditions for obtaining satisfactory deposits on copper are: bath composition: copper 63.5, sulphamate 197 g/l; pH 2; temperature 25°; limiting current density 7 A/cm<sup>2</sup>. The anode and cathode efficiencies achieved were close to 100%. The sulphamate bath is comparable to the sulphate and fluoborate baths for the electrodeposition of copper, except for its somewhat lower throwing power. [R.S.Sa.]

**933 - Controlled potential reactions of cadmium and silver in alkaline solution** (in English). G. T. Croft (Edison Laboratory, Thomas A. Edison Industries, McGraw-Edison Company, West-Orange, N.J., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 278-284.

The electrochemical oxidation and reduction of cadmium and silver in potassium hydroxide electrolyte were studied using two different methods at controlled electric tension: a fixed tension method and a sweeping tension method. It was found that the rate of oxidation of cadmium follows a parabolic growth law and that current maxima occur at the same over-tensions for both methods. These current maxima may be influenced by some indium added to the cadmium electrodes. From the results it may be inferred that the oxide growth is limited by transport of mass and electricity through the oxide layer. [H.Hur.]

**934 - Mechanism of electrodeposition of nickel from liquid ammonia solutions of spin-free nickel(II) complexes** (in English). G. W. Watt and D. A. Hazlehurst (Department of Chemistry, The University of Texas, Ausin, Texas, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 117-119.

Cathode current efficiencies for the electrolysis of ammonia solutions of hexaminenickel(II) bromide, trisethylenediaminenickel(II) bromide and bisdiethylenetriaminenickel(II) bromide were measured in the presence of potassium salts of  $Br^-$ ,  $I^-$  and  $SCN^-$ . For the metal deposit on the cathode it is assumed that a  $S_N2$  mechanism is operative. The reaction thus involves a nucleophilic attack by the added anion followed by the rupture of one of the original metal-ligand bonds. It is suggested that the bond breaking step is rate determining and depends on the relative transbilization effect of the entering ligand. [H.Hur.]

**935 - The significance of the Flade potential** (in English). M. J. Pryor (Metallurgical Laboratories, Olin Mathieson Chemical Corporation, New Haven, Conn., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 557-562.

A critical discussion of previous theories of the Flade electric tension is presented. A new theory is proposed. It is suggested that the electric tension-determining electrochemical reaction includes excess oxygen ions plus bound positive holes in the outer  $p$ -type layer of the  $\gamma$ - $Fe_2O_3$  passive film and hydrogen ions. When the  $p$ -type oxide has been removed, reaction proceeds on the  $n$ -type inner  $\gamma$ - $Fe_2O_3$  layer. The excess metal oxide in this inner region may react instantaneously in acid solutions (pH < 3) so that a shift in electric tension may occur which coincides with the end of the Flade plateau. At higher pH it is assumed that the ionic resistance of the  $n$ -type layer is reduced by hydroxyl ion exchange from the solution. This decrease of ionic resistance will also be accompanied by a shift in electric tension. [H.Hur.]

See also abstracts nos. 765, 776, 778, 887.

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