Vol. 56 OCTOBER, 1952 No. 7

THE JOURNAL OF PHYSICAL CHEMISTRY

(Registered in U. S. Patent Office)

Founded by Wilder D. Bancroft

SYMPOSIUM ON ELECTRON TRANSFER AND ISOTOPIC REACTIONS, NOTRE DAME, INDIANA, JUNE 11-13, 1952

Founded by Wilder D. Bancroft

THE JOURNAL OF PHYSICAL CHEMISTRY

(Registered in U. S. Patent Office)

Published monthly (except July, August and September) by the American Chemical Society at 20th and Northampton Sts., Easton, Pa.

Entered as second-class matter at the Post Office at Easton, Pennsylvania.

The *Journal of Physical Chemistry* is devoted to the publication of selected symposia in the broad field of physical chemistry and to other contributed papers.

Manuscripts originating in the British Isles, Europe and Africa should be sent to F. C. Tompkins, The Faraday Society, 6 Gray's Inn Square, London W. C. 1, England.

Manuscripts originating elsewhere should be sent to W. Albert Noyes, Jr., Department of Chemistry, University of Rochester, Rochester 3, N. Y.

Correspondence regarding accepted copy, proofs and reprints should be directed to Assistant Editor, Allen D. Bliss, Department of Chemistry, Simmons College, 300 The Fenway, Boston 15, Mass.

Business Office: American Chemical Society, 1155 Sixteenth St., N. W., Washington 6, D. C.

Advertising Office: American Chemical Society, 332 West 42nd St., New York 18, N. Y.

Articles must be submitted in duplicate, typed and double spaced. They should have at the beginning a brief Abstract, in no case exceeding 300 words. Original drawings should accompany the manuscript. Lettering at the sides of graphs (black on white or blue) may be pencilled in, and will be typeset. Figures and tables should be held to a minimum consistent with adequate presentation of information. Photographs will not be printed on glossy paper except by special arrangement. All footnotes and references to the literature should be numbered consecutively and placed on the manuscript at the proper places. Initials of authors referred to in citations should be given. Nomenclature should conform to that used in *Chemical Abstracts*, mathematical characters marked for italic, Greek letters carefully made or annotated, and subscripts and superscripts clearly shown. Articles should be written as briefly as possible consistent with clarity and should avoid historical background unnecessary for specialists.

Symposium papers should be sent in all cases to Secretaries of Divisions sponsoring the symposium, who will be responsible for their transmittal to the Editor. The Secretary of the Division by agreement with the Editor will specify a time after which symposium papers cannot be accepted. The Editor reserves the right to refuse to publish symposium articles, for valid scientific reasons. Each symposium paper may not exceed four printed pages (about sixteen double spaced typewritten pages) in length except by prior arrangement with the Editor.

Remittances and orders for subscriptions and for single copies, notices of changes of address and new professional connections, and claims for missing numbers should be sent to the American Chemical Society, 1155 Sixteenth St., N. W., Washington 6, D. C. Changes of address for the *Journal of Physical Chemistry* must be received on or before the 30th of the preceding month.

Claims for missing numbers will not be allowed (1) if received more than sixty days from date of issue (because of delivery hazards, no claims can be honored from subscribers in Central Europe, Asia, or Pacific Islands other than Hawaii) (2) if loss was due to failure of notice of change of address to be received before the date specified in the preceding paragraph, or (3) if the reason for the claim is "missing from files."

Annual Subscription: $8.00 to members of the American Chemical Society, $10.00 to non-members. Postage free to countries in the Pan American Union; Canada, $0.40; all other countries, $1.20. Single copies, $1.25; foreign postage, $0.15; Canadian postage $0.05.

* * * *(Continued from first page of cover)* * * *

CONTRIBUTED PAPERS

THE JOURNAL OF
PHYSICAL CHEMISTRY

(Registered in U. S. Patent Office) (Copyright, 1952, by the American Chemical Society)

Founded by Wilder D. Bancroft

VOLUME 56 OCTOBER 20, 1952 NUMBER 7

MOLECULAR COMPOUNDS AND THEIR SPECTRA. III. THE INTERACTION OF ELECTRON DONORS AND ACCEPTORS[1]

ROBERT S. MULLIKEN

Department of Physics, The University of Chicago, Chicago 37, Illinois

Received March 19, 1952

Extending earlier work,[2] a classification of electron acceptors and donors each into a number of types is given in Section II. In an extension of Sidgwick's nomenclature, donors D and acceptors A are here defined (see Section I) as all those entities during whose interaction transfer of negative charge from D to A takes place, with the formation as end-product either of an additive combination $A_m \cdot D_n$ or of new entities. In all cases of 1:1 interaction, the wave function ψ of A·D (and, formally at least, of the end-products also in the dissociative case) is of the approximate form given in equation (1) with appropriate ionic or covalent bonding (or no bonding) between D and A, and between D^+ and A^-, depending on whether A and/or D are closed-shell molecules or ions, or radicals.[3] Donors and acceptors as here defined correspond closely to nucleophilic and electrophilic reagents as defined by Ingold or, except for the inclusion here of donor and acceptor radicals, correspond rather well to bases and acids as defined by G. N. Lewis. In Section III, the applicability of an extension of eq. (1) to crystalline molecular compounds is considered briefly.[3] A brief discussion and listing of possible or probable known charge-transfer spectra[2,4] of donor–acceptor molecular complexes are given in Section IV and Table VI. Sections V–VIII contain further elucidation of matters discussed in Sections I–II and in ref. 2.

The energy U of interaction between a donor and acceptor as a function of a charge-transfer coördinate C (a kind of reaction coördinate, so defined as to increase from 0 to 1 with increasing transfer of electronic charge from D to A) is studied in Section IX for interactions between donor–acceptor pairs of the various classes defined here. In many cases, there should be two important minima in the $U(C)$ curve, namely, one for a loose "*outer complex*" for small C, and one for a tighter "*inner complex*," often of ion-pair character, for large C (see Figs. 1–2). In any particular case, one of these is the stable form, while the other is an excited or activated state (lower in energy, however, than the "activated complex" which usually intervenes between them). However, in many cases where the donor and acceptor form only a loose outer complex or none at all in the vapor state or in an inert solvent, the inner complex may become the stable form under the coöperative action of a suitable active solvent. The latter functions by solvation of the inner complex or its ions, either acting mainly electrostatically, or in some cases acting as (or, with the assistance of) an auxiliary acceptor or donor (double complex formation). The formation of ion-pair clusters or ionic crystals (*e.g.*, $NH_3 + HCl \rightarrow NH_4^+Cl^-$) can play the same role as that of an electrostatically functioning solvent in stabilizing the inner complex of a donor–acceptor pair. In a few interaction types, a "*middle complex*" is important (*cf.* Fig. 3), corresponding either to an activated complex or intermediate in a reaction such as those involving a Walden inversion, or to a stable association product as in I_3^- or HF_2^-. Section X contains improvements and errata for the previous papers of this series. The Appendix, consisting of Tables III–VI, contains detailed descriptions of the various donor and acceptor types and of their modes of functioning.

I. The Interaction of Donors and Acceptors

In chemical theory, the usefulness of G. N. Lewis's broad conception[5,6] of what should be meant by the words *acid* and *base* has become increasingly evident. However, since these words (especially *acid*) are commonly used with narrower meanings, it may be wisest to follow Sidgwick[7] in referring to Lewis acids and bases as (electron) acceptors and donors, respectively.[8]

---

[1] This work was assisted by the ONR under Task Order IX of Contract N6ori with The University of Chicago.

[2] II of this series: R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[3] See also Paper No. 25 in ONR Report on September, 1951, Conference on "Quantum-Mechanical Methods in Valence Theory." This Report is obtainable from L. M. McKenzie, Head, Physics Branch, Office of Naval Research, Department of Navy, Washington 25, D. C.

[4] I of this series: R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

[5] G. N. Lewis, "Valence and The Structure of Atoms and Molecules," The Chemical Catalog Company (Reinhold Publ. Corp.), New York, N. Y., 1923, pp. 142, 133, 113, 107; *J. Franklin Institute*, **226**, 293 (1938).

[6] W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946.

[7] N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929, in particular, p. 116, for the definition of donors and acceptors.

[8] For a valuable review, see R. P. Bell, *Quart. Rev. Chem.*, **1**, 113 (1947).

While Lewis's ideas grew largely out of inorganic chemistry, similar ideas were developed more or less independently in the field of organic chemistry, culminating in Lapworth's categories of anionoid and cationoid reagents, or Ingold's[9] of nucleophilic and electrophilic reagents. The latter correspond closely to Lewis bases and acids, respectively, except that they add reducing agents rather generally to the former and oxidizing agents to the latter. Usanovich[10] also proposed a similar classification. Luder and Zuffanti (ref. 6, Chap. 4) elaborated an approach similar to Ingold's, but substituted the term "electrodotic" for Ingold's "nucleophilic." They stated that "both acids (primarily in Lewis's sense) and oxidizing agents are electron acceptors," and "are electrophilic (reagents)"; and that "both bases and reducing agents are electron donors" and "are electrodotic (reagents)."

In defining basic and acidic molecules, Lewis (although his essential idea seems to have been distinctly broader) emphasized as characteristic the *sharing of an electron pair*, furnished by the base and accepted by *an atom* in the acid. Sidgwick adopted the same definition for donors and acceptors.

Ingold[9] said: "reagents which donate their electrons to, or share them with, a foreign atomic nucleus may be termed nucleophilic"; those "which acquire electrons, or a share in electrons, previously belonging to a foreign molecule or ion, may be termed electrophilic." Luder and Zuffanti (ref. 6) stated that "an acid accepts a share in an electron pair held by a base; an oxidizing agent takes over completely the electrons donated by a reducing agent," and made a corresponding statement regarding bases and reducing agents. It is proposed here to use Sidgwick's simple and almost self-explanatory terms "donor" and "acceptor" to mean essentially the same things as Ingold's "nucleophilic reagent" and "electrophilic reagent," or Luder and Zuffanti's "electrodotic reagent" and "electrophilic reagent."

More precisely, (electron) *donors* D and *acceptors* A are here defined as *all those entities such that, during the interaction between a particular species of D and a particular species of A entities, transfer of negative charge from D to A takes place, with the formation as end-products either of additive combinations or of new entities. The additive combinations may be 1:1, m:1, 1:n, or in general m:n combinations.*

This definition is one which becomes extremely natural when one attempts to express the familiar ideas of donor–acceptor interaction in quantum mechanical symbols.[2] The wave function ψ of the (stable or transitory) 1:1 complex A·D then takes in general the approximate form

$$\psi \approx a\psi_0(\mathrm{AD}) + b\psi_1(\mathrm{A^-D^+}) \qquad (1)$$

with appropriate ionic or covalent bonding (or no bonding) between A and D, and between A^- and D^+, depending on whether A and/or D are closed-shell molecules or ions, or radicals.[3]

Equation (1) describes the partial transfer of an electron from D to A; the ratio b^2/a^2 varies between 0 for no transfer and ∞ for complete transfer. Equation (1) does not necessarily demand either (1) sharing of an electron pair, or (2) that the transferred electron shall come strictly from one particular atom in D and go strictly to one particular atom in A. However, it does not exclude these as important special cases. Lewis's and Sidgwick's use of restrictions (1) and (2) in setting up their formal definitions of acids and bases, or acceptors and donors, though seeming natural at the time, has had some tendency to inhibit others from making the fullest or freest use of the inherent possibilities of the donor–acceptor concept. Also, without an explicit quantum mechanical formulation, the nature of *partial* electron transfer has tended to appear rather obscure; in particular, the validity of the donor–acceptor interaction concept for explaining the many loose organic molecular complexes has not always been seen in a clear light.[2]

Ingold's definitions dropped the first of the two limitations in Lewis's, but did not clearly dispose of the second. The present definition, as given above in words and in quantum mechanical form, definitely drops both. In dropping the second limitation, it permits one, when this is appropriate, to think in terms of intermolecular donor–acceptor action between molecules as wholes—an idea which may be considered as a slight generalization of one used by Dewar in connection with his concept of π-complexes.

The simple quantum mechanical viewpoint expressed in eq. (1) makes clearer the justifiability of the inclusion by Ingold and others of bases and reducing agents in a single class (donors) and of Lewis acids and oxidizing agents in another (acceptors). It goes further in indicating that there is perhaps even no fundamental need in terms of theory to distinguish bases and reducing agents as subclasses of the class "donor" or Lewis acids and oxidizing agents as subclasses of the class "acceptor." These distinctions now appear as perhaps matters of practical convenience rather than of basic theory. However, the question of course deserves much more thorough consideration. A point to be kept in mind is perhaps the fact that the terms "oxidation" and "reduction" are generally used for over-all processes, and often in more or less formalistic ways with respect to assignments of charges to atoms; whereas very often (not always) the concepts of Lewis acids and bases (or electrophilic and nucleophilic reagents) are used in connection with (real or supposed) actual mechanisms of reactions.

In terms of Lewis's definition calling for the sharing of an electron pair, acceptors such as BF_3 and H^+ (if it existed free) were clear cases of typical acids. Oddly enough, Lewis appears to have found it a little awkward to include the H-acids, for example HCl, as acids at all *per se* (that is, in the absence of ionizing solvents)—as can be inferred

[9] C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934), especially pp. 265, 273; *J. Chem. Soc.*, 1120 (1933), especially the footnote on p. 1121.

[10] Usanovich in 1939 (see ref. 6, p. 14, for a summary in English) defines an acid as any substance capable of giving up cations or of combining with anions, and a base as any substance capable of giving up anions or of combining with cations.

from Lewis's 1938 paper,[5] and from Luder and Zuffanti's book.[6]

Luder and Zuffanti describe H-acids HQ as secondary acids, in the sense that, while they are not really Lewis acids themselves, they are capable of supplying a Lewis acid (namely H^+) to a base. [That is, they are donors of the Lewis acid H^+, or proton donors.] These secondary Lewis acids are thus thought of as composites of a primary Lewis acid (H^+) and a base (Q^-); and in a similar way various other composites of real or conceivable primary Lewis acids and bases can be described as secondary Lewis acids. (The same or similar composites could equally be described as secondary bases.) For example, various covalent compounds RQ, likewise such typical compounds of primary Lewis acids and bases as $H_3N \rightarrow BMe_3$, may be considered as secondary Lewis acids (or as secondary bases). (See also Table VI, footnote *d.*) The matter of the classification of H-acids and various other molecules RQ as acceptors will be discussed rather thoroughly below.

Meanwhile, it may be noted that Ingold had no hesitation in classifying molecules such as HQ and RQ as electrophilic reagents. (From a similar point of view, Usanovich classified HQ and RQ as acids.[10]) In so doing, Ingold pointed out briefly (ref. 9, p. 269) that electrophilic reagents can be subdivided into classes in various ways, one such subdivision being into two types which may be called associative acceptors (*e.g.*, BF_3) and dissociative acceptors (*e.g.*, HQ or RQ).

In a preceding paper,[2] a classification of donors and acceptors into a number of distinct types was outlined. This has been somewhat revised, extended, and clarified in Tables I–VI below. Using this classification, the present formulation (like Ingold's) seems among other things to make it easier to treat under a unified scheme and viewpoint the action of one and the same donor molecule in such different activities as are expressed by, for instance

$$H_2O + BF_3 \longrightarrow H_2O \rightarrow BF_3 \qquad (2)$$

and

$$H_2O + HCl \xrightarrow{aq} H_3O^+aq + Cl^-aq \qquad (3)$$

The first action (with a good L-acid) is purely associative, the second (with a good H-acid) is an ionogenic displacement reaction; from the viewpoint of the H-acid acceptor, it is dissociative. What the two reactions have in common is (1) partial transfer of an electron from the donor H_2O to the acceptor, and (2) formation of a (somewhat incomplete, or partial) dative bond between the donor and the acceptor. In the second reaction, of course, an additional thing happens: namely, splitting of the acceptor, during the acceptation process, into an ion Cl^- and a (partially positive) H atom, it being the latter, rather than the acceptor as a whole, which unites covalently with the (strongly positively charged) H_2O to form the dative bond.[11]

While the commonly used description of the second reaction as a proton transfer reaction is very convenient, it is open to two criticisms: (1) it is only formal or schematic, in the sense that at no time during the process of transfer is the proton really more than partially free from an electron (in other words, the proton carries a large fraction of an electron with it during its transfer); (2) it ignores the important fact of concurrent partial electron transfer from the H_2O. If (2) is ignored, the fruitful possibility of a unified common classification of the two reactions as electron donor–acceptor reactions is thrown away. A more detailed analysis of reaction (3) is given in Section VII.

Here it may further be noted that Luder and Zuffanti in describing H-acids as secondary Lewis acids have adopted the same proton transfer viewpoint as was used by Brønsted and Lowry. In the present viewpoint (as also apparently in Ingold's concept of electrophilic reagents), the H-acids HQ, together with other molecules RQ, are classified directly as acceptors in their own right along with primary Lewis acids, such as BF_3. According to this viewpoint, while it is true that an acceptor like HCl can be regarded formally as a compound of another acceptor H^+ and a donor Cl^-, physically according to quantum mechanics the structure is believed to be much more nearly covalent than ionic.

Since in ordinary chemistry the free ion H^+ does not occur (though to be sure it can exist in gas discharges), it appears to be more realistic to classify it as a virtual than as an actual acceptor under normal conditions.

II. The Classification of Donors and Acceptors and Their Interactions

A general classification of donors and of acceptors each into several fairly well-marked types is given in Tables III and IV in the Appendix; each type is there characterized in detail. An orienting survey is given in Table I in this Section. A general scheme displaying the chief modes of interaction of some of the most important donor–acceptor pair types is presented in brief condensed form in Table II, and in detail in Table V in the Appendix. Table V is supplemented in Table VII in the Appendix by a listing of numerous individual examples, together with remarks in the case of certain pair-types about special features of their behavior. The examples include cases of molecular complex formation (D·A), molecular compound formation (D→A), and bimolecular displacement reactions (A + D → B + C) between donors D and acceptors A. (The use of the words "complex" and "compound" here is not intended as a definitive proposal.)

The notation used in the Tables is rather fully explained in their footnotes, but a few general remarks about it here may be worth while. First of all, the symbols have been chosen with considerable care to be as simple and brief as is consistent with making them reasonably self-explanatory, convenient for speaking, writing or printing, and free from possibilities of confusion with other symbols likely to be used in the same context.

---

(11) How best to describe what happens in reactions like (3) has of course long been a moot question. See for example ref. 7, pp. 68, 114, on the similar case of NH_3 + HCl.

TABLE I

TYPES OF DONORS AND ACCEPTORS[a]

1. Donors (D)

Major Types:	n (onium)	$b\pi$ (π donor)	$b\sigma$ (σ donor)	R (radical)
Some sub-types:	n (neutral onium) n' (onium anion)			

2. Acceptors (A)

Major Types:	v (vacant-orbital)	π	σ	Q (radical)
Some sub-types:	v (neutral v) v^* (v cation)	$x\pi$ (π) $k\pi$ (ketoid π)	$x\sigma$ (halogenoid σ) $h\sigma$ (H-acid) $k\sigma$ (σ) $h\sigma^*$ (cationic H-acid) $k\sigma^*$ (σ cation)	

[a] For further details, including subclassification according to associative and dissociative modes of functioning (denoted by subscripts a and d, respectively), see Tables III and IV in the Appendix (see also Table II). The n donors and v acceptors always function associatively.

While the broad categories of "donor" and "acceptor" denote modes of functioning, it is convenient to divide donors and acceptors each into classes based on their structure before interaction. The first broad division of donors is into even lone-pair or onium (n and n'), even bonding-electron (π and σ), and odd-electron (R) radical donors. Similarly, acceptors are classified as even vacant-orbital (v and v^*), even bonding-electron (π, σ and σ^*), and odd-electron (Q) radical acceptors. The individual classes mentioned (there are also others, but those mentioned are the most important) can conveniently be further divided in some cases into subclasses (for example, the σ acceptor subclass $h\sigma$ consists of all neutral molecule H-acids). The boundaries between classes (or subclasses) are not always sharp, because the structures of actual donors and acceptors are often more or less intermediate between those of two or more classes (see, for example, Table IV, Remarks column). It should also be noted that the same molecule, especially if it is a large molecule with various parts, may function under different circumstances sometimes as one kind of a donor, sometimes as another; or again as one or another type of acceptor. For example, even so small a molecule as H_2O functions on occasion either as an n donor or as an $h\sigma_d$ acceptor; and probably sometimes as a $b\sigma_d$ donor, or even perhaps in other ways.

For each of the structure-based classes or subclasses of donors and acceptors, there is at least one, and there are often two, characteristic modes of functioning or behavior. When there are two modes of functioning, one of these is associative, the other is dissociative (indicated by a and d in Table II). In Tables III–VI in the Appendix, these are symbolized by adding subscripts (a or d) to the class or subclass symbol. The combined symbols are then regarded as denoting subclasses or sub-subclasses. For some classes or subclasses, only the associative, or else only the dissociative, mode is usual.

For a given donor or acceptor functioning in the dissociative mode (this most often occurs only in the presence of "environmental coöperation," that is, assisting electrostatic or other forces or agencies, for example, those due to an ionizing solvent: see Section VI), one of its covalent bonds is broken, commonly in a displacement reaction in which ions are formed or exchanged. Actual separation of the atoms or ions formerly joined by the broken covalent bond does not necessarily occur, however. It does *not* occur when the π bond of a double bond is broken ($b\pi_d$ donors, and $k\pi_d$ acceptors), since a σ bond then always remains. Even in the case where a σ bond (single bond) is broken, if two ions are formed, they may still cohere if in the presence of a non-ionizing solvent or in the vapor state (but they are seldom formed under these circumstances), or if in an ionic crystal; commonly, however, they become separated by the process of electrolytic dissociation in an ionizing solvent.

TABLE II

MAJOR DONOR-ACCEPTOR REACTION TYPES

Donor Types	Acceptor Types							
	v	v^*	$x\pi$	$k\pi$	$x\sigma$	$h\sigma$	$k\sigma$	$h\sigma^*$ and $k\sigma^*$
n	aa	aa	aa	ad	aa ad_s	ad_s	ad_s	ad_r
n'	aa	aa	aa ad	aa ad	aa	aa ad_r	ad_r	ad_r
$b\pi$	aa	aa da	aa	aa	aa dd_s	aa dd_s		
$b\sigma$	da_s	da_r			aa			

Explanation. For each entry in the table, the first symbol refers to the donor, the second to the acceptor. The symbol a denotes associative, d dissociative, behavior. In associative behavior of a donor or acceptor, all the original bonds remain unbroken (and in some cases a new bond is formed). In dissociative behavior of σ donors or acceptors, a single bond (σ bond) is broken during the reaction; for π donors or acceptors, the π component of a double bond is broken, but since a single bond then remains, the link is not split. Processes involving dissociative behavior usually require environmental assistance (*cf.* Section VI). The subscript s denotes that a salt (undissociated or dissociated) is formed. The subscript r means that a displacement reaction occurs. In all cases where there is no subscript, the donor and acceptor cohere upon interaction. (However, often the product may react further.) For further details, see Tables V and VI.

For a donor or acceptor functioning in the associative mode, a new covalent bond, either incipient (in loose complexes) or more or less fully developed, and either interatomic or intermolecular, is formed. Only lone-pair donors and vacant-orbital acceptors are capable of functioning in the associative mode to form strong fairly fully developed new covalent bonds. When bonding-electron (σ and π) donors or acceptors function associatively, it is only with a loosening (partial breaking) of their bonds; if the interaction becomes really strong (usually under environmental coöperation), it passes over into the dissociative mode, with more or less complete rupture of one bond.

The class and subclass symbols have been so chosen that they can be simplified, adapted, or extended in various ways according to convenience. For example, one may speak of $b\pi$ reagents, or of $b\pi$ or simply π donors; one may speak of $x\sigma$ acceptors, or collectively of σ acceptors (including $x\sigma$, $h\sigma$, $k\sigma$, $l\sigma$, $h\sigma^*$, and $k\sigma^*$, acceptors), or collectively of σ_d acceptors. The notations v^* and σ^* for unipositive cation acceptors and n' for anion acceptors can readily be extended to multiply charged ions (*e.g.*, v^{**}, v^{***}, n'', $x\pi^*$, etc.). The superscripts * and ′ have been used, rather than $^+$ and $^-$, because in some discussions one may wish to refer to donors and acceptors of these types to or from which electrons have been added or subtracted (for example, n'^+ or v^{*-}).

Finally, it should be pointed out that several changes, believed to be considerable improvements, have been made in the notation used in previous papers.[2,4] Among other changes, D (for "donor") has been substituted for B (which suggests "base"), and the acceptors formerly called d have now become the subclasses $x\sigma$, $h\sigma$, and $k\sigma$ of the σ class of acceptors.

It should be emphasized that the classification scheme as here proposed is still more or less tentative and incomplete. In particular, the classes R and Q and their interactions have been treated only sketchily. It should also be emphasized that the primary purpose of the detailed Tables in the Appendix is not to attempt an authoritative classification of actual molecules and reactions, but rather to give probable or plausible examples to illustrate the functioning of the various donor and acceptor types. The writer hopes he may be forgiven if some of the examples appear unrealistic to experts who are much more familiar than he with the relevant experimental facts.

Time alone can show just how useful a detailed classification such as that given here may be, or to what extent, or in what areas or what connections, this or a similar classification may have value.

III. Loose Molecular Complexes in the Solid State

The structure of any loose 1:1 molecular complex or compound between *neutral closed-shell entities* can be described in terms of wave functions essentially as[2]

$$\psi_N \approx a\psi_0(D, A) + b\psi_1(D^+{-}A^-) \qquad (1a)$$

where $\psi_0(D, A)$ represents a no-bond structure and $\psi_1(D^+{-}A^-)$ a dative structure for the donor-acceptor pair D, A. A more general expression not limited to neutral closed-shell entities has already been given at the beginning of Section I as eq. (1).

Equation (1a) is easily generalized to cover n:1 and other cases.[2] The fact that solid crystals are abundantly known[12] with the same 1:1 (or in general m:n) composition as for individual molecules of complexes in solution or in vapor can also be understood. It is only necessary to assume that even in such a crystal (the same applies also to an individual n:1 or m:n complex) the predominant intermolecular forces are local, pair-wise, donor-acceptor interactions between each donor molecule and its nearest sufficiently near acceptor neighbors, and between each acceptor molecule and its nearest sufficiently near donor neighbors. This assumption is quantum mechanically entirely reasonable, and it appears safe to take the fact of the very frequent occurrence of complexes in solution and as crystalline solids with the same stoichiometric composition, as very strong empirical evidence of its correctness. Further evidence from the spectra of solid complexes will be reviewed in Section IV. Coöperative effects involving more remote neighbors (and finally the entire crystal) must also of course exist, but apparently these are of secondary importance in typical cases.

As has been pointed out previously,[2,3] donor-acceptor interactions, even though relatively weak, should exist also in molecular crystals built from a single molecular species, and often these forces should have orientational properties. In particular they should tend to cause aromatic molecules to be stacked in such a way that the planes of adjacent molecules, although often parallel, are displaced from being directly superposed.[13] This is what is observed in the crystals both of aromatic molecules of a single species and of aromatic molecular complexes. Such molecules are often stacked like a pack of cards along an axis, but with the planes of the molecules all inclined to the stacking axis.[14] Examples of the two cases are the crystals of hexamethylbenzene (stacking angle 44°27′) and quinhydrone (1:1 quinone–hydroquinone; stacking angle 34°). On the other hand, for the crystals of $(CH_2Br)_6C_6$ (hexabromomethylbenzene) the molecules are strung directly above one another along the axis (stacking angle 0°). This is understandable on the basis of steric effects, including the fact that the bromine atoms are so big as to keep the benzene planes much farther apart than in hexamethylbenzene and thus greatly to reduce the charge-transfer orientational forces.

In a recent Letter,[15] Abrahams has pointed out that in crystalline p-nitroaniline, an oxygen atom of a nitro group of one molecule is abnormally close to a carbon of the benzene ring of a neighboring molecule; and he attributes this to donor–acceptor interaction. This example falls under the $b\pi_a,x\pi_a$ interaction type (*cf.* Table II, and Section 11 of Table VI), but is of special interest in indicating rather strongly localized donor–acceptor interaction. As has been suggested to the writer by Dr. H. McConnell, this action (for any pair of interacting molecules) can be understood in terms of a major charge transfer resonance component in which the N atom of the NH_2 group of one

---

[12] P. Pfeiffer, "Organische Molekülverbindungen," 2nd edition, F. Enke, Stuttgart, 1927

[13] Reference 2, Secs. VII, VIII; and J. Landauer and H. McConnell, *J. Am. Chem. Soc.*, **74**, 1221 (1952).

[14] K. Nakamoto, *ibid.*, **74**, 390, 392, 1739 (1952). These papers include a convenient brief survey of several examples illustrating the modes of packing of aromatic molecules in crystals.

[15] S. C. Abrahams, *ibid.*, **74**, 2692 (1952).

molecule donates an electron to the N atom of the NO_2 group of a neighboring molecule. Assuming this charge transfer, an orthoquinoid arrangement of the π bonds in the first molecule then permits a new intermolecular covalent link to be formed between one of the two ring carbons ortho to the amino nitrogen and an oxygen of the nitro group of the second molecule. Presumably the 1:1 and 2:1 $b\pi_a,x\pi_a$ solution complexes of aniline with the polynitrobenzenes involve a similar sort of partially or largely localized π–π donor–acceptor interaction.

IV. Charge Transfer Spectra

As has been pointed out previously,[2] if eq. (1a) represents the ground state N of a 1:1 molecular complex, there must also exist an excited state E with

$$\psi_E \approx a^*\psi(D^+\text{–}A^-) - b^*\psi(D, A) \qquad (4)$$

Then if, for example, the ground state has predominantly no-bond structure ($a^2 \gg b^2$), this excited state must have predominantly dative structure. It was also pointed out that on the basis of quantum mechanics the absorption spectrum of the complex must include (in addition to the individual spectra of D and A, somewhat modified by their interaction) a band (normally in the visible or ordinary ultraviolet) corresponding to an absorption jump from state N to state E, and characteristic of the complex as a whole. This was called an intermolecular charge transfer spectrum. Especially notable is the fact that the theory predicts the possibility of highly intense charge transfer absorption even for very loose complexes.[2]

As a prime example, the intense absorption near λ2900 in the spectra of the loose complexes of benzenoid hydrocarbons with molecules of the halogens was discussed in detail in ref. 2. Tentative identification of an intense ultraviolet absorption of solutions of iodine in ethyl ether as being a charge transfer spectrum of an ether–iodine complex was also made.[4] Work just completed by Mr. J. S. Ham in this Laboratory, showing that this spectrum definitely belongs to a 1:1 ether–iodine complex, supports this view. Mr. Ham has also measured a new ultraviolet absorption in the spectrum of solutions of iodine in *t*-butyl alcohol, and has identified it as a charge transfer spectrum of a 1:1 complex.

During the past year, other investigators (especially Andrews and Keefer) have published several papers on molecular complexes and their spectra, in which equilibrium constants were determined and which revealed the possible or probable presence of charge transfer spectra. The wave lengths of a number of such spectra are listed under the appropriate complexes in Table VI, together with literature references. In many cases, the charge transfer identification was mentioned tentatively by the authors of the papers cited.

In addition, there are numerous less recent papers on organic complexes in which color changes have been noted, and a few for which spectra have been mapped. Further, attention should be called to the absorption spectra of inorganic complexes and ions in solution and in crystals, a subject briefly reviewed by Rabinowitch in 1942.[16] Most of the spectra of stable complex anions such as NO_3^-, CH_3COO^-, MnO_4^-, and of complex cations of similar stability, may best be considered as normal molecular spectra, but it may be noted that normal molecular spectra include *interatomic* charge transfer spectra.[17] In addition, anions in solutions, in particular simple ions like Cl^-, contain spectra which have long been attributed to electron transfer from the anion to environing molecules, but to which Platzmann and Franck have recently given a new and rather different interpretation.[18] Earlier (1926), Franck and collaborators had shown that the absorption spectra of alkali halide vapors correspond to an interatomic electron transfer process. Still earlier, the concept of electron transfer was used in interpreting the spectra of ionic crystals.[16] The high intensity short wave length absorption spectra of many of the less stable cations and anions in solution have been described by Rabinowitch as electron transfer spectra.[16]

In the earlier work, it was supposed that electron transfer spectra occur only corresponding to transfer of an electron from a negative ion (or perhaps an electron donor like H_2O—*cf.* Table V of ref. 16) to a positive ion. The more recent work[17,2] corresponds to a broader concept in which electron transfer spectra may occur corresponding to electron transfer between any two atomic or molecular entities, even if these are uncharged. It appears probable that a re-examination of the structure and spectra of complex ions from the present point of view will be very fruitful.

Returning to the organic complexes, a recent paper by Nakamoto[14] is of particular interest. Nakamoto examined long wave length spectra which appear to be the charge-transfer spectra of certain 1:1 crystalline molecular complexes (among others, quinone:hydroquinone), in polarized light. For 1:1 complexes between aromatic or unsaturated π donors and π acceptors, the theory[2] predicts that the electric vector should be polarized with a large component perpendicular to the planes of two interacting adjacent molecules which are parallel to each other, and this is what Nakamoto found. As was pointed out in Section III, it is reasonable to suppose that the charge transfer forces in such crystalline complexes act essentially pairwise between neighboring molecules. The spectra should then be similar to those for individual 1:1 complexes in solution, although appreciably modified by cooperative effects involving non-neighbor molecules. Thus Nakamoto's work appears to support both the charge transfer interpretation of the characteristic spectra of molecular complexes, and the idea of primarily pairwise-acting charge transfer forces in crystalline complexes.

A further point of interest is that in aromatic crystals composed of a single molecular species (*e.g.*, hexamethylbenzene), although the stacking of the molecules at an angle to the stacking axis

---

[16] E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942). Review on electron transfer and related spectra.

[17] R. S. Mulliken, *J. Chem. Phys.*, **7**, 201 (1939), and later papers, especially R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics* (London Physical Society), **VIII**, 231 (1941).

[18] R. Platzmann and J. Franck, *L. Farkas Memorial Volume*.

(*cf.* Section III above) is explainable by charge transfer forces (and no other explanation is evident), there is in the longer wave length part of the spectrum no charge transfer absorption band like that for quinone–hydroquinone. This is theoretically not unreasonable, since for self-complexes[13] the charge transfer forces should be much weaker, and the charge-transfer absorption in general much weaker and at shorter wave lengths, than for the much stronger complexes between unlike molecules. Whether, however, the existence of sufficiently strong charge transfer forces to account for the stacking of the molecules of a self-complex at a considerable angle is quantitatively compatible, in terms of theory, with the absence of any indication of a charge transfer spectrum, is a matter which should be investigated further. Meantime, it may be useful to assume this compatibility at least as a guiding hypothesis in further experimental studies.

V. The Strengths of Donors and Acceptors

The factors determining the strengths of donors and acceptors in the formation of relatively loose addition complexes have been discussed previously.[2,3] The importance of low vertical ionization potentials I^{vert} for strong donors, and of high vertical electron affinities E^{vert} for strong acceptors, was stressed. It was pointed out that I^{vert} and E^{vert} should be taken corresponding to a nuclear skeleton which is that of the actual complex. This is a compromise (often a severe one) between the often very different skeletal structures that would occur for molecules with electronic structures corresponding to the separate resonance components ψ_0 and ψ_1 of eq. (1a). The importance of other factors, in particular mutual approachability, in determining interaction strengths, was also emphasized. For example, approachability is especially good between n (or n') donors and v (or v^*) acceptors, or between π donors and π acceptors, but not between π donors and v acceptors.

When donors and acceptors interact not in the associative but in the dissociative mode, the factors determining donor and acceptor strengths are altered considerably. Leaving aside entropy factors for the moment, the important factors can be seen by writing equations for the various terms involved in the net heat of reaction. For ionogenic displacement reactions like (3), one immediately finds that low I (here not I^{vert}) values are favorable for good donors, and high E (not E^{vert}) for good acceptors.

Specifically, for the reaction of an associative donor D with a dissociative σ acceptor RQ

$$\text{D} + \text{RQ} + sl \longrightarrow \text{DR}^{+}sl + \text{Q}^{-}sl \qquad (3a)$$

the heat of reaction is evidently

$$\left.\begin{aligned} &E_{\text{Q}} + H_{\text{Q}^-} + H_{\text{DR}^+} + (B_{\text{DR}^+} - B_{\text{RQ}}) - I_{\text{D}} \\ &= (H_{\text{DR}^+} + B_{\text{DR}^+} - I_{\text{D}}) + (H_{\text{Q}^-} - B_{\text{RQ}} + E_{\text{Q}}) \end{aligned}\right\} \qquad (3b)$$

where the B's denote bond dissociation energies and the H's solvation energies. Similarly, for the reaction of a dissociative σ donor RQ with an associative acceptor A (*e.g.*, a v acceptor)

$$\text{RQ} + \text{A} + sl \longrightarrow \text{R}^{+}sl + \text{QA}^{-}sl \qquad (3c)$$

the heat of reaction is

$$\left.\begin{aligned} &E_{\text{A}} + H_{\text{R}^+} + H_{\text{QA}^-} + (B_{\text{QA}^-} - B_{\text{RQ}}) - I_{\text{R}} \\ &= (H_{\text{R}^+} - B_{\text{RQ}} - I_{\text{R}}) + (H_{\text{QA}^-} + B_{\text{QA}^-} + E_{\text{A}}) \end{aligned}\right\} \qquad (3d)$$

In eqs. (3b) and (3d), it is not $I_{\text{D}}^{\text{vert}}$ and $E_{\text{A}}^{\text{vert}}$ which matter, but I_{D} and E_{Q} in the former, I_{R} and E_{A} in the latter. The difference between the energy of the bond which is formed and that which is broken also has some influence. It is easily seen why solvation of the ions is so often the decisive factor in making ionogenic reactions possible.

As stressed by Lewis,[5] it is not feasible to arrange bases and Lewis acids into unique orders of strength valid for all Lewis acid–base reactions. It is usually concluded as a corollary that it is futile to try to arrange donors or acceptors in any universally valid quantitative orders of strength, except for acid and base strengths in the familiar case of H-acids interacting with bases in solutions. However, with the present classification of donors and acceptors into a number of fairly well-marked types, perhaps it will be worth while to see whether roughly quantitative scales of donor and acceptor strength can be set up for the interactions of donors of a particular type with acceptors of a particular type; and then to look for different scales for other pairs of types.

VI. Conditional and Unconditional Donor and Acceptor Behavior[19]

Beyond the classifications already mentioned, donor–acceptor reactions may be characterized as either unconditional or absolute (occurring between the members of the donor–acceptor pair without assistance, for example, in vapor or in inert solvents); or as conditional or contingent (requiring the presence of environmental coöperation).

Environmental coöperative action[20] may take various forms, among which it will be convenient to distinguish two principal cases. One of these, designated "es" in Tables I–VI (see footnote *c* of Table III), is that of essentially electrostatic environmental action. In the other, two molecules coöperate in reacting as acceptors with a third molecule as donor, or *vice versa* (for examples, see Tables V, VI).

Usually "es" involves either attachment of solvent molecules to the donor–acceptor reaction product (that is, solvation; usually with dissociation into solvated ions), or else polymerization (formation of ion-clusters in solution, or of an ionic crystalline solid). The role of es in conditional reactions is to stabilize the reaction products sufficiently to make the reaction possible.

Dissociatively functioning donors ($b\pi_{\text{d}}$ and $b\sigma_{\text{d}}$ donors) and acceptors (π_{d}, σ_{d} and σ^*_{d} acceptors) seldom behave dissociatively without environmental coöperation; in other words, they are *usually* conditional.

---

[19] For a general survey of reaction rates and mechanisms, especially in solution, reference may be made to L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, and to Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[20] See also E. D. Hughes' discussion (*Trans. Faraday Soc.*, **34**, 185 (1938)) of "constitutional effects . . ." and "environmental effects in nucleophilic substitution."

It will be noted that the terms "conditional" and "unconditional" describe alternative modes of functioning of donors and acceptors, just as do the terms "dissociative" and "associative," introduced in Section II and indicated in Tables V–VI by subscripts d and a. It would therefore be appropriate to add further subscripts, say c and u, for conditional and unconditional modes, respectively, leading to symbols such as $x\sigma_{\mathrm{ua}}$, $x\sigma_{\mathrm{cd}}$, $h\sigma_{\mathrm{cd}}$, etc. In most cases, however, only one of the alternatives u or c occurs for any one donor or acceptor class and a or d subclass, and so these subscripts have been omitted in the symbols in the Tables.

Nevertheless under some circumstances, to indicate special types of conditional functioning, it may at times prove useful to employ subscript symbols. Symbols such as $x\sigma_{\mathrm{cd}}$, $x\sigma_{\mathrm{es,d}}$, $x\sigma_{\mathrm{vd}}$, $x\sigma_{\mathrm{sl,d}}$, $x\sigma_{\mathrm{xt,d}}$, are therefore suggested to denote, respectively, conditional functioning of unspecified character, of electrostatic character, of auxiliary v-acceptor character, of solvent character (which in turn may be of pure es, donor or acceptor, or mixed, character), and ionic-crystal-es character; with at the same time dissociative functioning in all.

The n' donors and the v^* and d^* acceptors, being ionic, are seldom encountered except under es conditions. However, in Tables III and IV, this fact has been embodied in the definitions of these types. For example, the anionic chlorine donor is defined as $\mathrm{Cl^-}$es, which may mean $\mathrm{Cl^-}$ surrounded by $\mathrm{Na^+}$ (and so on) in a crystal, or $\mathrm{Cl^-}$ attached to a single $\mathrm{Na^+}$ in vapor or in an inert solvent, or hydrated $\mathrm{Cl^-}$ ($\mathrm{Cl^-}$aq) in water solution. With these definitions, n' donors and v^* and d^* acceptors are here regarded as usually unconditional.

A further point is that the "es" in an n' donor or v^* acceptor is intended in general to have qualitative rather than quantitative meaning, so that, for example, it is not necessary to account for a fixed number of water molecules when a $\mathrm{Cl^-}$aq donor reacts.

Another related point is the fact that when an ion is solvated, the solvating solvent molecules may function either in a purely es role as discussed in the two preceding paragraphs, or in a more or less strongly donor or acceptor role as, for example, the two $\mathrm{NH_3}$ in $\mathrm{Ag^+(NH_3)_2}$aq, and the $\mathrm{SO_2}$ in $\mathrm{Cl^-SO_2}$. If the solvent molecules function definitely as donors or acceptors, they are conceived of here as forming integrated structural parts of larger entities, such as, for example, the σ^*_{d} acceptor $\mathrm{Ag^+(NH_3)_2}$aq, or the σ'_{d} donor $\mathrm{Cl^-SO_2}$. In practice, of course, border-line cases are frequent. In such cases, it may be best to be guided by convenience, and to some extent custom, even at the risk of arbitrariness. For example (*cf.* Table IV), $\mathrm{Ag^+}$aq is most conveniently regarded as a v^* acceptor, rather than as a σ^*_{d} acceptor like $\mathrm{Ag^+(NH_3)_2}$aq, even though it may be that the σ^*_{d} classification would be closer to the truth. Similarly, $\mathrm{Cl^-SO_2}$ may often conveniently be regarded like $\mathrm{Cl^-}$aq as an n' rather than as a σ'_{d} donor. On the other hand, it is probably unwise to class the typical stable σ^*_{d} acceptor $\mathrm{H_3O^+}$aq as a v^* acceptor ($\mathrm{H^+}$aq).

Conditional σ_{d} acceptors (σ_{cd} acceptors) like HQ or RQ are, *by themselves*, strictly speaking, not acceptors or Lewis acids at all; it is really not they, but HQ plus es or RQ plus es, which function as σ_{cd} acceptors. The usual omission of reference to es may be considered as a convention adopted in the interest of simplicity. It is particularly important to remind oneself of this when using the ordinary concept of H-acids, a concept of whose very existence this tacit convention is an intrinsic part.

Some types of donors and acceptors typically function only unconditionally, and others only conditionally. Acceptors of the $x\sigma$ subclass, however, although unconditional when functioning associatively ($x\sigma_{\mathrm{ua}}$ acceptors), often act in the presence of ionizing solvents as conditional acceptors ($x\sigma_{\mathrm{cd}}$ acceptors). Thus if iodine is dissolved in water, it seems probable that unconditional formation of the loose reversible $n\cdot x\sigma_{\mathrm{a}}$ complex $\mathrm{H_2O\cdot I_2}$ first occurs, very rapidly; and that then, with the es assistance of water, reaction occurs over an activation barrier to a structure $\mathrm{H_2OI^+I^-}$ (of $n\rightarrow x\sigma_{\mathrm{d}}$ type), thence to $\mathrm{H_2OI^+}$es + $\mathrm{I^-}$es; whereupon the σ^*_{d} acceptor $[\mathrm{H_2OI}]^+$es is attacked by the n donor $\mathrm{H_2O}$ to form $\mathrm{HOI} + \mathrm{H_3O^+}$aq; and so on. There seems to be evidence that in this complex and reversible series of donor–acceptor reactions, the iodine is present predominantly as $\mathrm{H_2O\cdot I_2}$. In the example just discussed, it will be noted that the water acts sometimes in an es role, sometimes as an n donor.

VII. Detailed Comparison of Dissociative and Associative Donor–Acceptor Reactions

To clarify further the brief comparison in Section I between associative and dissociative charge transfer reactions, it is instructive to follow each of the reactions eq. (2) and (3) through from beginning to end in terms of a varying linear combination of two resonance structures ψ_0 and ψ_1 of the kind specified in eq. (1a). In both reactions, a of eq. (1a) decreases and b increases as the reaction proceeds. To make matters fully clear, additional details are needed to describe the metamorphoses, during reaction, of the internal structures of the original donor and acceptor in ψ_0 and of their ions in ψ_1.[11,19]

For reaction (3), eq. (1a) becomes

$$\psi_{\mathrm{N}} \approx a\psi_0(\mathrm{H_2O,HCl}) + b\psi_1(\underset{\text{aq}}{\mathrm{H_2O^+{—}HCl^-}}) \tag{4}$$

Here the formulation in terms of $\mathrm{HCl^-}$ is admittedly artificial, especially since $E^{\mathrm{vert}} \ll 0$ in the first stages of the reaction (see Table VI, discussion under reaction-type 14). Actually, with detailed resonance structures given as in (5) below, no mention of $\mathrm{HCl^-}$, or of ψ_0 or ψ_1, is really essential. However, the introduction of the concepts which these respresent is valuable in showing the parallelism between reactions (2) and (3).

Neglecting some minor resonance structures, and leaving to be tacitly understood the presence and es action of the solvent, reaction (3) must go somewhat as follows

$$
\begin{array}{l}
\psi(\mathrm{H}^{+0.4}\mathrm{H}^{+0.4}\mathrm{O}^{-0.8},\ \mathrm{H}^{+0.2}\mathrm{Cl}^{-0.8}) = \psi_0(\mathrm{H_2O,\ HCl}) = \\[4pt]
\qquad \psi_0: \left\{\begin{array}{llll} 0.8\ \mathrm{H_2O} & & \mathrm{H}\text{———} & \mathrm{Cl} \\ 0.2\ \mathrm{H_2O} & \cdots\cdots\cdots & \mathrm{H^+}\cdots & \mathrm{Cl^-} \end{array}\right\} \longrightarrow \\[4pt]
\left\{\begin{array}{l}
\psi_0: \left\{\begin{array}{lllll} 0.39\ \mathrm{H_2O} & \longleftrightarrow & \mathrm{H}\text{————} & & \mathrm{Cl} \\ 0.35\ \mathrm{H_2O} & \cdots\cdots & \mathrm{H^+} & \cdots\cdots & \mathrm{Cl^-} \end{array}\right\} \\
\psi_1: \left\{\begin{array}{lllll} 0.25\ \mathrm{H_2O^+} & \text{——} & \mathrm{H} & \longleftrightarrow & \mathrm{Cl^-} \\ 0.01\ \mathrm{H_2O^+} & \cdots\cdots & \mathrm{H^-} & \longleftrightarrow & \mathrm{Cl^-} \end{array}\right\}
\end{array}\right\} \longrightarrow \qquad (5) \\[4pt]
\qquad \left\{\begin{array}{lll} 0.5\ \psi_0: \mathrm{H_2O}\cdot\cdot & \mathrm{H^+}\cdots\cdots\cdots & \mathrm{Cl^-} \\ 0.5\ \psi_1: \mathrm{H_2O^+{—}H} & \cdots\cdots\cdots & \mathrm{Cl^-} \end{array}\right\} = \\[4pt]
\psi(\mathrm{H}^{+0.5}\mathrm{H}^{+0.5}\mathrm{O}^{-0.5}\mathrm{H}^{+0.5}\cdots\cdots\cdots\mathrm{Cl}^{-1}) = \\
\qquad\qquad \psi(\mathrm{H_3O^+}\cdots\cdots\cdots\mathrm{Cl^-}) = \psi[(\mathrm{H_2O})^{+0.5}(\mathrm{HCl})^{-0.5}].
\end{array}
$$

The numbers preceding the individual resonance structures are rough estimates or guesses of their relative weights. The symbols —, · · ·, and ←→ indicate covalent bonding, electrostatic attraction.

and non-bonded repulsion, respectively. The first and last lines contain various types of summary of the estimated detailed charge distributions in the initial and final stages.[21]

A comparison between various formulations of the initial and final stages in (5) permits various descriptions of the over-all effects of the reaction. One point which is interesting is that although the H_2O molecule as a whole donates an estimated 0.5*e* to (the two parts of) the HCl, the O atom in H_2O donates only 0.3*e* of this, and moreover still remains negatively charged in the final ion H_3O^+. Also, the Cl atom, in attaining its final charge of $-1.0e$, starts with an estimated $-0.2e$ taken from its original partner, picks up a further $-0.3e$ from this partner during the action, and gains $-0.5e$ more from the original H_2O, of which the O supplies $-0.3e$ and the two hydrogens each $-0.1e$.

In scheme (5), the intermediate stage shown probably represents an activated state. In an analogous formulation of some of the other reactions in Table VI (see in particular reaction-types 13, 14 and 17 there), the intermediate stage certainly corresponds to an activation barrier over which the reaction proceeds slowly (rate measurements have been made in many examples). The fact that reactions such as $H_2O + HCl \rightarrow H_3O^+Cl^-$ do not occur in the vapor phase probably means that without solvent or crystallization assistance the final fully ionic stage of the reaction, although presumably lower in energy than the intermediate activated state, would be higher in energy than the initial stage before reaction. The way in which the energy varies with degree of reaction would then correspond to curve I in Fig. 1, below (see Section IX for a further analysis).

For comparison with (5), a similarly formulated description of the initial and final stages of reaction (2) is given in (6). Again the reader is warned that the estimated numbers are uncertain (though enlightened) guesses.

$$\begin{gathered}\psi(H^{+0.4})_2O^{-0.8},\ B^{+1.8}(F^{-0.6})_3 \Rightarrow \underset{\text{planar}}{\psi_0(H_2O,\ BF_3)} \longrightarrow \\ \left\{\begin{matrix} 0.2\psi_0\text{: } H_2O \cdots BF_3 \\ 0.8\psi_1\text{: } H_2O^+ \overset{}{\underset{\cdots}{—}} BF_3^- \end{matrix}\right\} = \\ \psi(H^{+0.6})_2O^{-0.4},\ B^{+1.3}(F^{-0.7})_3 = \underset{\text{pyramid}}{\psi[(H_2O)^{+0.8}(BF_3)^{-0.8}]}\end{gathered} \qquad (6)$$

The fact that $H_2O \cdot BF_3$ is an extremely powerful H-acid, *i.e.*, $h\sigma_d$ acceptor, yielding, with a base D, DH^+es + $(HOBF_3)^-$es, is readily understandable if the charge distribution in the final product is somewhat as shown.

VIII. Symmetrization

Attention should be called briefly to a familar phenomenon which is characteristic of the final stages of many donor–acceptor interactions. When for instance a donor of structure R_nZ interacts with a $k\sigma_d$ acceptor of structure RQ to give $R_{n+1}Z^+ + Q^-$, the original donor and acceptor at first approach without special cognizance of the common possession of R atoms; but during the last stages of the reaction, more or less internal readjustment takes place in the R_nZ structure in such a way that all $n + 1$ R atoms become equivalent, with some extra gain in stability thereby. Processes of this kind and of the type $RQ + YQ_n \rightarrow R^+ + YQ_{n+1}^-$ may be called *symmetrization* processes. Some typical examples (sl = solvent) are

$$\left.\begin{aligned} &RX + BX_3 \longrightarrow R^+sl + BX_4^-sl \\ &n\,XR + n\,NR_3 \longrightarrow (NR_4^+X^-)_n \text{ solid} \\ &Cl^-aq + ICl \longrightarrow ICl_2^-aq \\ &Br^-sl + AlCl_3 \longrightarrow AlCl_3Br^-sl \end{aligned}\right\} \qquad (7)$$

The last example is typical of the frequently occurring phenomenon of partial, or near, symmetrization.

IX. Inner, Outer and Middle Complexes

Energy of Donor–Acceptor Pair as Function of Charge Transfer Coördinate.—In a general consideration of the possible modes of interaction of a D,A (donor–acceptor) pair, it is instructive to plot the energy of interaction *U* against a reaction coördinate *C*. Without defining it precisely, let *C* be a quantity which increases continuously with charge transfer (that is, with *b*/*a* in eq. (1a)), subject to the added specification that the nuclear skeleton be so adjusted for each value of *C* as to make *U* as small as possible. Thus *C* may be called a charge transfer reaction coördinate, or simply a charge transfer coördinate.

A convenient scale for *C* runs from $C = 0$ for $b/a = 0$ (D and A not yet in contact) to $C = 1.0$ for some state of maximum charge transfer. Figures 1 and 2 show several plausible forms for $U(C)$, in which the left-hand minimum of *U* may be taken as defining $C = 1$, while in the region at the right, $C \rightarrow 0$ as D and A separate and $U \rightarrow 0$. For those curves in which a maximum of *U* occurs between $C = 0$ and $C = 1$, the position of this maximum may conveniently be taken as defining $C = 0.5$.

As will be shown below, Figs. 1 and 2, or variations on them, are probably applicable to most D–A interaction types. For a few types, however, the $U(C)$ curves must look like those in Fig. 3, and it is then convenient to define *C* as ranging from -1 through 0 to $+1$ as *b*/*a* goes from 0 to 1 to ∞.

As compared with the geometrically defined reaction coördinates used by Eyring, Polanyi and others, the charge transfer coördinate *C* is less concrete in that it is based on theoretical quantities which are not accurately known. Further, one cannot be sure that the normal path of every charge transfer reaction has to be one in which *C* steadily increases; however, geometrically defined reaction coördinates are not necessarily free from a similar difficulty. In any event, *C* is extremely convenient for present purposes, in that by its use the degree of completion of a donor–acceptor reaction is described in terms of a single coördinate.

Inner and Outer Complexes.—The broad division of the modes of functioning of donors and

---

(21) The structure $H_2O^+ \cdots H^- \leftrightarrow Cl$, with estimated coefficient only 0.01 in the intermediate stage in (5), is mentioned here since, although unimportant in this example, analogous structures should be of considerable importance in general (for example, in $H_2O + I_2$ and other $n + x\sigma_d$ reactions (*cf.* Table VI)). The importance of this structure relative to $H_2O^+{-}H \leftrightarrow Cl^-$ is probably at a maximum at the beginning of the reaction (c nearly zero).

acceptors into associative and dissociative was discussed in Sections II and VI. It is useful at this point to introduce a further, derived, concept. Donor–acceptor *pairs* may be said to be functioning associatively if both partners are functioning associatively, or dissociatively if (at least) one partner is functioning dissociatively.

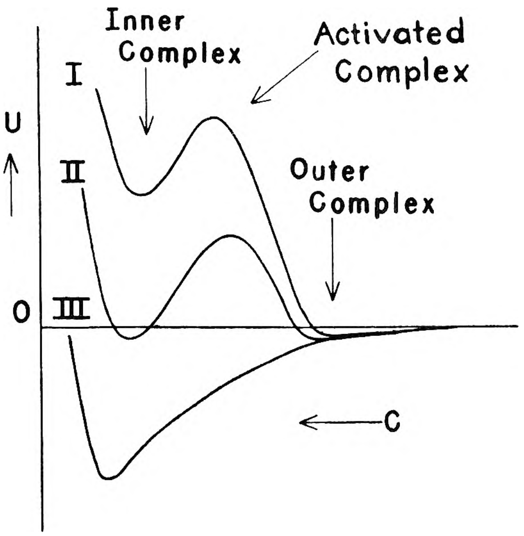


Fig. 1.—Energy curves $U(C)$ for unassisted interaction (inert solvent or none) between a donor D and an acceptor A. (Qualitative only; C = reaction coördinate, increasing from 0 toward 1 as b^2/a^2 in eq. (3) increases.) The "outer complex" (C small) corresponds to $b^2 << a^2$, the "inner complex" ($C = 1$) to $b^2 \approx a^2$ or $b^2 > a^2$, and the "activated complex" ($C = 0.5$) is intermediate.

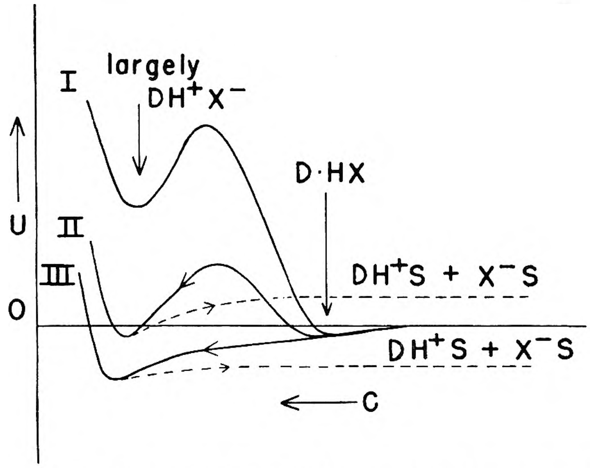


Fig. 2.—Energy curves $U(C)$ for assisted interaction between a donor D and a σ_d acceptor HX (the curves would be similar for Group 3, 4 or 5 D,A pairs in general): curve I, unassisted; curve II, same assisted by a weak and rather low-dielectric solvent (dotted branch of curve is for dissociation of DH^+X^-S into solvated ions (S = solvent)); curve III, like curve II but for strong and high-dielectric solvent.

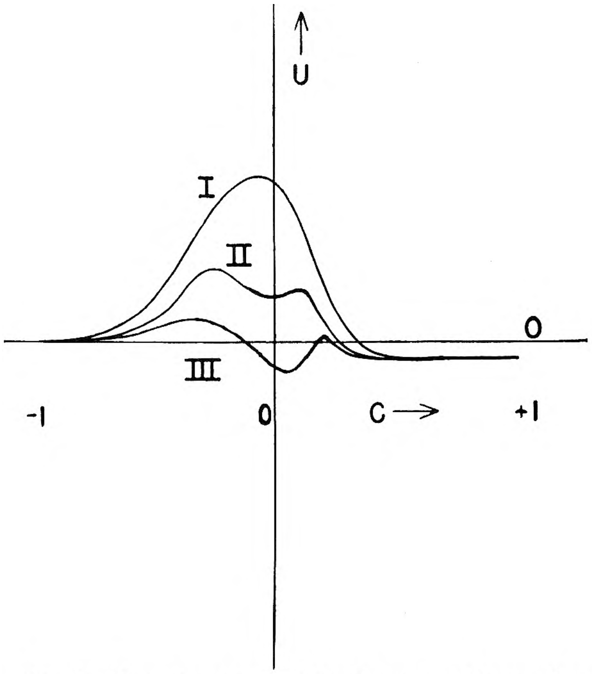


Fig. 3.—Energy curves $U(C)$ for charge transfer reactions of the type of eq. (8) and (9). "Middle complex" near $C = 0$ of curve III. $C = -1$, 0 and $+1$ here correspond more or less to $C = 0$, 0.5 and 1 of Figs. 1 and 2. In each curve, shallow depressions (outer complexes—*cf.* Figs. 1 and 2) near $C = \pm 1$ are an additional possibility.

Table II gives a survey of the usual observed behaviors of important types of D,A pairs. Behavior aa (see Table II) is associative. All other behaviors (ad, da and dd) are dissociative; it may be recalled here that dissociative functioning usually occurs only with environmental assistance. Pairs in which the donor is of class n or n' and the acceptor of class v or v^* function only associatively; these will be called Group 1. For all other types of D,A pairs, either associative or dissociative functioning is in principle possible, and is frequently realized (see Table II). Among these latter types, dissociative functioning involves in some cases typical displacement reactions other than salt formation (subscript r in Table II); these will be called Group 2. In others it involves ion-pair (salt) formation (subscript s in Table II); these will be called Group 3. In still others (Groups 4 and 5) it involves formation of an addition product in which the dissociative action is the breaking of a π bond of a double bond, leaving a σ bond, however, so that the atoms formerly linked by the double bond are still held together. Group 3 includes the important types $n + \sigma$ and $b\pi + \sigma$ (see Sections 13, 14, 18, 19 of Table VI); some examples are

$$NH_3 + HCl \longrightarrow NH_4^+Cl^- \text{ (or } NH_4 + Cl^- \text{ in solution)}$$
$$Ar + HF + BF_3 \longrightarrow ArH^+BF_4^- \text{ in HF solution}$$

In Group 4 (types n or $n' + \pi$, *cf.* Section 9 of Table VI), internal ionization occurs, while in Group 5 (type $b\pi + v^*$, *cf.* Section 7 of Table VI), an ionic complex or intermediate of considerable stability is formed.

A review of the behavior patterns just outlined and of other experimental facts suggests that those for Groups 3, 4 and 5 can be understood in terms of $U(C)$ curves similar to those shown in Figs. 1 and 2, with associative action corresponding to the shallow *"outer complex,"* dissociative action to the deeper *"inner complex,"* and with in general an *"activated complex"* corresponding to the maximum between these minima. Later in this Section, qualitative quantum theoretical reasoning will be presented in support of curves of the general forms indicated, but the discussion immediately following will be more in terms of empirical evidence.

The curves of Fig. 1 are intended to apply to D,A interactions *without* environmental assistance. Among the curves in Fig. 1, curve I may be fairly typical for Groups 3, 4 and 5, while curve III (with no distinction between inner and outer complex) is probably typical for stable Group 1 pairs (Groups 1 and 2 will be discussed further at the end of this Section). Figure 2 is intended to apply to D,A interactions of Groups 3, 4 and 5 with varying degrees of environmental assistance. Variations on Figs. 1 and 2 are of course also to be expected, including cases with almost no outer complex, or with no inner complex, or with an additional small activation barrier outside the outer complex.[22]

To make it more definite, Fig. 2 has been labeled to correspond to a Group 3 D,A pair. Curve I in Fig. 2 (which is essentially the same as curve I in Fig. 1) may be taken as typical for the case of little or no environmental coöperation. Curves II and III may then represent the same D,A pair in the presence of two degrees of strong environmental influence, for example of the electrostatic influence of a polar solvent. The shift from a curve like I to one like II or III is just what is to be expected under the influence of a polar environment, since such an environment must lower the energy *more and more as C increases*, since increasing C corresponds to increasing ionic character in the wave function. If the environmental influence is sufficiently strong, the inner complex may become the stable form of the D,A pair when with less or no environmental influence the outer complex (or the separate molecules) may represent the stable form.

If the inner complex becomes the energetically more stable form, more or less complete separation into solvated ions may thereupon occur as a secondary process (dashed curves in Fig. 2) if the assisting agent is an ionizing solvent. This electrolytic dissociation may be regarded as taking place with C essentially constant at the value 1 if the inner complex ($C = 1$) already corresponds to maximum charge transfer and 100% ionic character. (The C scale thus is not applicable to the dashed curves.)

If the assisting process is ionic-crystal formation (*e.g.*, $NH_3 + HCl \rightarrow NH_4^+Cl^-$ crystal), it is a sort of polymerization rather than a separation of the ions which takes place. Curves II and III, but not the dashed curves, are now still more or less applicable. The process is still "dissociative" in the basic sense used here that a covalent bond originally present is broken.

The fact that for a given D,A pair under a particular set of environmental conditions one usually observes *either* an inner complex *or* an outer complex is understandable in terms of Figs. 1 and 2. The further fact that, if environmental conditions are suitably varied, many D,A pairs can be found to exhibit either associative (outer complex) or dissociative (inner complex) behavior is also readily understandable in terms of Fig. 2 and the discussion given above. To make matters more explicit, examples of each of the main D,A pair types which can function dissociatively will now be considered (for further examples, see Table VI).

The known experimental facts on the Group 3 D,A pair $NH_3 + HCl$ (type $n + h\sigma$) are consistent with Fig. 2 using a type I curve for the vapor state and a type III curve for this pair either in solution in a polar solvent (say, liquid ammonia), or in a crystal (solid $NH_4^+Cl^-$). As is well known, solid $NH_4^+Cl^-$ on vaporization gives a vapor consisting of unassociated NH_3 and HCl molecules[23]; it has also been shown that if thoroughly dry NH_3 and HCl gases are brought together at room temperature, they do not react to form $NH_4^+Cl^-$ crystals.[24] These facts are understandable if the energy of the unassisted $NH_4^+Cl^-$ inner complex of curve I is so high that the number of such ion-pairs in equilibrium with $NH_3 + HCl$ vapor at room temperature is too small to lead to the formation of crystal nuclei.

It may, however, be assumed on theoretical grounds that some small fraction of the molecules at any moment are associated in the form of an $H_3N{\cdot}HCl$ outer complex which should be held together by weak $N \cdots H$ hydrogen bonding plus dispersion forces. Theoretical considerations indicate, however, that such outer complexes as may exist for $NH_3 + HCl$ and other D,A pairs of the types $n + h\sigma$, $n + k\sigma$, $\pi + h\sigma$, and $\pi + k\sigma$, are *not* stabilized to any appreciable extent by *charge transfer forces;* in other words, that $C = 0$ for such outer complexes. A further discussion of these points is given in the introductions to Sections 14 and 19 of Table VI.

The system $H_2O + HCl$ should be similar to NH_3

---

[22] An example of the last-mentioned case is the loose I_2·propylene associative complex concerning which Freed and Sancier (*J. Am. Chem. Soc.*, **74**, 1273 (1952)) report that iodine in solution at 77°K. in propane, an inert solvent, upon addition of propylene, develops the color of the iodine·propylene complex only slowly, indicating a small outer barrier.

[23] See. W. H. Rodebush and J. C. Michalek, *J. Am. Chem. Soc.*, **51**, 748 (1943).

[24] According to Spotz and Hirschfelder (*J. Chem. Phys.*, **19**, 1215 (1951)), NH_3 and HCl gases on mixing react to form Liesegang rings of solid $NH_4^+Cl^-$, but the authors' theoretical analysis indicates that there must be a clustering of very large numbers of D,A pairs before crystals begin to form. More recently, W. H. Johnston and P. J. Manno have reported (*Ind. Eng. Chem.*, **44**, 1304 (1952)) that no reaction at all occurs, even after hours of waiting, between thoroughly dried NH_3 and HCl gases.

These results may be understood as follows. In terms of Fig. 2, a single $NH_4^+Cl^-$ ion-pair would correspond to the high-energy inner complex of curve I. If enough such ion-pairs could be clustered together, their mutual electrostatic attractions would lead to curves of lower and lower energy (per pair) until, at some critical cluster size, some curve (perhaps one similar to II) would be reached, for which the cluster would be big enough to grow spontaneously. Actually, however, any extensive clustering (and this would be rare) would have to be in the first instance of *molecule-pairs* $H_3N{\cdot}HCl$ (outer complexes); and it is clear that the activation energy barring the way to a simultaneous transformation of enough of these to ion-pairs would probably be so high that it could not ordinarily occur at an appreciable rate. On the other hand, it is understandable that H_2O molecules should assist clustering and reduce the activation energy for transformation to an $NH_4^+Cl^-$ cluster, although it is not at all clear why water vapor should be quantitatively adequate to produce precipitation of solid $NH_4^+Cl^-$.

Consideration of curve I for $NH_3 + HCl$ leads to the interesting possibility that at sufficiently high temperatures and pressures, gaseous $NH_3 + HCl$ may contain a large proportion of $NH_4^+Cl^-$ ion-pairs.

+ HCl, but since H_2O is a weaker base than NH_3, the energy of the ion-pair inner complex (structure $H_3O^+Cl^-$) in the vapor system might be expected to be still higher than for NH_3 + HCl. In a polar solvent (say, H_2O), however, the inner complex evidently is sufficiently stabilized so that all the HCl + H_2O goes over to this form (and at the same time dissociates into ions). But in contrast to the D,A pair NH_3 + HCl, the stability of the inner complex is here evidently not sufficient to permit formation of an ionic crystal. In other words, even an infinite clustering of $H_3O^+Cl^-$ monomers does not bring curve I of Fig. 2 down quite low enough—although presumably it comes rather close to doing so.

The D,A pair ethyl ether plus iodine (I_2) is an example of the Group 3 type $n + x\sigma$ for which the existence (in solutions in inert solvents) of an outer complex stabilized by charge transfer forces seems to be well established by spectroscopic evidence.

In the case of another $n + x\sigma$ D,A pair, namely, pyridine (Py) plus iodine in the rather polar solvent pyridine,[2] there is satisfactory evidence for ionization into $(PyI)^+$ and I^-, indicating inner complex formation. Here the electrical conductivity increases slowly with time, indicating a slow approach toward equilibrium by passage from outer to inner complex *over a barrier of considerable height*, in harmony with a $U(C)$ curve similar to II of Fig. 2. Further, the limiting conductivity varies with dilution, again suggesting a definite equilibrium between Py,I_2 pairs in an outer complex (here it seems reasonable to suppose a *rapid* equilibrium $Py + I_2 \leftrightarrows Py{\cdot}I_2$) and in an inner complex ($PyI^+I^-sl \rightleftarrows PyI^+sl + I^-sl$).

It seems probable that the system $H_2O + I_2$ in water solution involves a similar but much more rapid set of equilibria (plus side equilibria). References on the D,A pairs just discussed are given in Table VI, Section 13.

Continuing with Group 3 examples, there is good evidence for the existence, in non-polar solvents, of loose outer complexes between $b\pi$ donors (*e.g.*, benzene and the alkylbenzenes) and σ acceptors of all subclasses ($h\sigma$ acceptors, *e.g.*, HCl; $k\sigma$ acceptors, *e.g.*, methyl alcohol; and $x\sigma$ acceptors, *e.g.*, I_2 and other halogens). Just as for $n + \sigma$ D,A pairs, however, it is very probable from theoretical considerations that the $b\pi$ outer complexes observed with $h\sigma$ and $k\sigma$ acceptors are hydrogen bonded and not charge transfer complexes; whereas for the $b\pi{\cdot}x\sigma$ outer complexes, there is abundant spectroscopic evidence that these are true charge transfer complexes. (See Table VI. Sections 18 and 19, for further discussion and references on outer complexes of the $b\pi + \sigma$ types.)

Further, it is rather well established (*cf.* Table VI, Section 19) that with suitable environmental coöperation, $b\pi$ donors with σ acceptors form salts which conform completely to the idea of inner complexes as outlined in this paper. These salts (either as ion-pairs, or dissociated) probably exist as reaction intermediates momentarily present in low concentration, or in some cases as stable entities reversibly producible. Illustrative of the $b\pi + h\sigma$ inner complexes are those formed from the alkylbenzenes and the hydrogen halides with an auxiliary acceptor (this action may be regarded as one type of environmental coöperation—see Section VI)

$$Xy + HF + BF_3 \rightleftarrows (XyH)^+BF_4^- \text{ in HF solution}$$

$$Tol + HCl + AlCl_3 \rightleftarrows (TolH^+)AlCl_4^- \text{ in toluene solution}$$

where Xy means xylene; Tol, toluene. In the first of these reactions, the v acceptor BF_3, plus the polar solvent HF, furnish the environmental coöperation which stabilizes the inner complex $(XyH^+)F^-$ of Xy and HF.

[**Digression on Double Charge Transfer Reactions.**—Reactions in which there is an auxiliary acceptor may be thought of either as assisted dissociative charge transfer reactions, as has been done above, or as dissociative "double charge transfer reactions." The latter description is appropriate because there is partial charge transfer from a donor molecule to both of the two acceptor molecules involved.

It is worth noting explicitly here that in such reactions each molecule is behaving typically in its donor or acceptor role. Thus in the first reaction, Xy functions as a dissociative donor, in the sense that one of the original π bonds is broken. (More accurately stated, there is a breaking up of the original aromatic resonance, such that the main resonance structures in the carbonium ion XyH^+ contain two π bonds instead of three.[25]) Further, the acceptor HF functions dissociatively in the same way as if it had reacted with an n donor, such as NH_3; but with the additional circumstance that the resulting F^-, instead of remaining free, becomes simultaneously an n' donor toward the v acceptor BF_3.]

There seems to be every reason to believe that $k\sigma$ and $x\sigma$ acceptors can under suitable conditions function in the same way as $h\sigma$ acceptors toward aromatic hydrocarbons; for example, that an ionic inner complex may exist as an intermediate in the dry chlorination of, say, benzene, as shown

$$Bz + Cl_2 + FeCl_3 \longrightarrow [(BzCl^+)(FeCl_4^-)] \longrightarrow PhCl + HCl + FeCl_3$$

The foregoing examples have all been from Group 3. Turning to Group 5, the interaction of $b\pi$ donors with v^* acceptors apparently can likewise give rise to either outer or inner complexes (see Table VI, Section 7). Thus Bz (benzene) forms what appears to be an outer complex with Ag^+ and similar v^* acceptors, under suitable conditions of environmental assistance; for example, when $Ag^+ClO_4^-$ is dissolved in Bz, the complex is formed in the presence of the ClO_4^- which presumably remains in the ion-pair $(Bz{\cdot}Ag^+)ClO_4^-$. Here the Ag^+ is believed not to be on the symmetry axis of the Bz but to be held, relatively loosely, above the middle of one C–C bond of the ring.[2] On the other hand, in certain solutions in polar solvents, Bz is believed to react with v^* acceptors present in small concentrations, *e.g.*, NO_2^+sl in sulfuric acid solution, or R^+sl in certain other solutions (R^+ denoting

---

(25) However, there is partial restabilization, probably strong, of the carbonium ion by hyperconjugation of the π system with the CH_3 or similar group in XyH^+ (see forthcoming LCAO MO calculations on BzH^+ by L. W. Pickett in coöperation with the author).

an alkyl carbonium ion), to form reaction intermediates such as $(BzNO_2)^+$sl and $(BzR)^+$sl, in which undoubtedly the added radical becomes attached by a fairly normal bond to one carbon of the Bz. The resulting carbonium ion presumably has the same kind of structure as BzH^+ discussed above, in which in effect one of the original π bonds has been broken, so that the carbonium ion is an inner complex in the same sense as for D,A pairs of types $b\pi + h\sigma$ or $b\pi + k\sigma$. In fact, if we disregard the accompanying anions, the same inner complex is in principle obtainable from a $b\pi + k\sigma$ reaction as from a $b\pi + v^*$ reaction, in case the $k\sigma$ acceptor is of a structure RQ which can ionize to form R^+ and Q^- freeing the R^+ to function as a v^* acceptor. If H^+ were capable of actual existence as a v^* acceptor, a similar comparison could be made between $b\pi + h\sigma$ and $b\pi + H^+$. Comparing the reactions $Bz + Ag^+$ and the hypothetical $Bz + H^+$, one notes that the former gives an outer complex, the latter would give an inner complex, the difference doubtless being explainable in terms of the difference in relative strengths of Ag and H bonds and in the sizes of the Ag^+ and H^+ ions. [ADDED IN PROOF.—Possibly another model for BzH^+, with the H^+ located above and between two ring carbons (*cf.* $Bz{\cdot}Ag^+$) should also be considered. In a recent conversation, M. Dewar advocates this model.]

The plausibility of the postulated forms of the $U(C)$ curves in Fig. 2 on the basis of the experimental evidence has now been shown. A qualitative proof that they are also in agreement with theoretical expectations from quantum mechanics will now be undertaken.

The theory of the formation of outer complexes by charge transfer forces has been given in ref. 2 (for a brief review, plus some extensions, see Sections I, IV and V above). In the important case of closed-shell donors and acceptors, the theory is based on the idea that as a donor and an acceptor come (or are forced) more and more closely together, the initial no-bond function $\psi_0(D,A)$ becomes increasingly admixed with a dative function $\psi_1(D^+—A^-)$. Taken by itself, ψ_0 would give a steadily increasing exchange repulsion for increasingly close approach.[26] If, however, the corresponding repulsion energy at first rises sufficiently slowly, it may be temporarily overcome by resonance between ψ_0 and ψ_1 so that a charge transfer outer complex is formed.

But if the energy of ψ_1 is too high relative to that of ψ_0, or the matrix element of energy for the resonance of ψ_0 and ψ_1 is too small, the charge transfer forces may be too weak to give rise to an outer complex. Theoretical considerations indicate that this situation occurs for certain Group 3 D,A pairs (n and $b\pi$ donors with $h\sigma$ and $k\sigma$ acceptors) where the acceptors have no (or a negative) electron affinity. However, outer complexes nevertheless often occur in such cases as a result of other forces, in particular hydrogen bonding (see specific discussion of examples of Group 3 D,A pairs in preceding paragraphs). In other Group 3 cases where the acceptor has an appreciable electron affinity (n and $b\pi$ donors with $x\sigma$ acceptors), outer complexes definitely attributable to charge transfer forces occur.

At distances of approach closer than those for the outer complex, $U(C)$ should at first rise with decreasing distance because of the predominance of ψ_0. However, even in cases where the charge transfer forces are slow in getting started, they must eventually come into play; that is, C increases above zero, ψ_1 mixes more and more into ψ_0, and resonance between ψ_0 and ψ_1 begins to cut down the rate of energy rise. Finally there must come a point where ψ_1 begins to predominate over ψ_0. The fact then becomes important that the energy of ψ_1 decreases with decreasing separation of D and A—up to the point where relevant atoms come within normal bond distances of each other, after which, of course, it increases. In view of these facts, it is readily seen that the energy may be expected to go over a maximum (activated complex) and then fall to a minimum corresponding to the inner complex. In this way, $U(C)$ curves like curve I in Fig. 2 are seen to be in agreement with theoretical expectations for D,A pairs interacting without environmental coöperation. Simple theoretical arguments given earlier then show that, with suitable environmental coöperation, curve I should be replaced by curves like II and III.

Although the reasoning just given is generally applicable for donors and acceptors capable of functioning dissociatively, and having closed-shell structures, certain additional details regarding the dissociative process are also relevant. These can be explained in terms of an example. For this, the case of $H_2O + HCl$, examined in Section VII (see especially eqs. (5) there) is useful. The qualitative discussion which follows is equally applicable to the unassisted D,A pair or to the same pair under environmental assistance. (In Section VII, solution in water was assumed.)

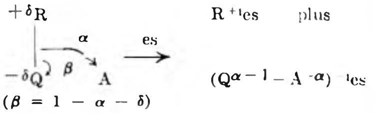
It is convenient to begin by supposing the HCl to be placed near the H_2O with the H directly between the Cl and the O, and with the Cl at a distance from the O approximately equal to that in the (ionic but undissociated) inner complex or reaction product $H_3O^+Cl^-$. For this state of affairs, C would still be only a little larger than zero. If now C is allowed to increase, the H atom moves toward the O atom. The O–Cl distance, though regulated by the specification that it so adjust itself as to keep U as low as possible for any value of C, very likely remains nearly constant. As C increases, U tends to increase because (1) the non-bonded repulsions within ψ_0 (see eqs. (5)) increase; (2) the amount (b^2/a^2) of the higher-energy wave function ψ_1 increases. On the other hand, the following factors work increasingly to *diminish* U as C increases: (1) *electrostatic polarization* within ψ_0 (that is, increase of the $H_2O \cdots H^+ \cdots Cl^-$ resonance component within ψ_0); (2) decrease in the energy of ψ_1 because of increasing attractions and decreasing repulsions as the H moves toward the O atom; (3) decrease in the energy of ψ_1 because of

---

(26) In complex formation in general, valence bond rearrangements such as can occur without charge transfer (as, *e.g.*, in $H_2 + I_2 \rightarrow 2HI$) should also, at close approach, contribute to cutting down U, by resonance.

TABLE III

ELECTRON DONOR (D) TYPES[a]

Symbol	Name	Essential Structure[b, c]	Nature of Donor Action[c]: General Character	Nature of Donor Action[c]: VB Description[d]	Nature of Donor Action[c]: MO Description[d]	Examples
n	Onium donor	Neutral even system containing relatively easily ionized atomic lone pair	Association for valency increase	Partial dative transfer (*cf.* eq. (1a)) from lone pair, as follows $n + A \rightarrow \text{Res.}\left\{\begin{matrix} n, A \\ n^{+}\text{—}^{-}A \end{matrix}\right\}$	$n{:} + A \rightarrow n{:}\,A$	Amines, alcohols, ethers, ketones, nitriles, CO, sometimes halides, sometimes SO_2
n'	Onium anion donor	Even ion Q^- or usually Q^-es containing easily ionized atomic lone pair	Same as n	Same as n	Same as n	Es-solvated anions[c] of H-acids, *e.g.*, I^-, CH_3COO^-, OH^-, NH_2^-
$b\pi$	π donor	Neutral even system containing easily ionized bonding π electrons	$b\pi_a$: loose dative association $b\pi_d$: Strong dative association essentially with formation of one σ bond and loss of one π bond	$b\pi_a$: Partial dative transfer of electron from any π bonding pair, with resonance of donor action among all π electrons	$b\pi_a$: Partial dative transfer of electron from pair occupying most easily ionized bonding π MO	Aromatic (Ar) and unsaturated (Un) hydrocarbons, and their substitution products with electron-releasing substituents
$b\sigma$	σ donor	Neutral even system RQ with rather weak and polar R–Q bond (polarity R^+Q^-)	$b\sigma_a$: Loose dative association (rare) $b\sigma_d$: Ionogenic displacement reaction, usually es-assisted	$b\sigma_d$: Partial dative transfer of electron from R–Q bonding pair to acceptor with accompanying partial transfer of electron R → Q, and liberation of R^+:  		Alkyl and aralkyl halides, esters, etc., especially if R^+ is resonance-stabilized; also solid metals (*e.g.*, Na, Mg, Cu)
R	Radical donor (reducing radical)	System with relatively easily ionized odd electron				Univalent metal atoms, H atom, alkyl, aralkyl, and other easily ionized radicals

[a] See Section II for general explanation. [b] "Essential Structure" refers of course, in complicated cases, only to the region where the donor or acceptor action takes place. [c] The symbol es (*cf.* Section VI) denotes the presence of a source of electrostatic forces which stabilizes the system in question: usually an attached polar solvent molecule or molecules, or sometimes a companion ion or ions, as in ion-pairs, ion-clusters, or solid salt. [d] VB means valence bond; MO means molecular orbital. Res. denotes resonance between the structures indicated.

"dative polarization" (that is, readjustment of the relative proportions of the resonance components—probably increase of H_2O^+—H ↔ Cl^- relative to $H_2O^+\cdots H^-$ ↔ Cl, the latter being probably at maximum importance near $C = 0$)[21] within ψ_1; (4) resonance between ψ_1 and ψ_0.[26] The net outcome of the factors outlined should probably be $U(C)$ curves like those in Fig. 2, perhaps like I for no environmental assistance and like II or III in the presence of such assistance.

The *n,v* Molecular Compounds.—The Group 1 D,A pairs (see Sections 1, 2 and 5 in Table VI) fall into a rather different behavior class from the Group 3–5 pairs so far considered. They comprise *the* typical donor–acceptor pairs of Lewis and Sidgwick, for which direct association yields a stable datively-bonded addition product. Here curves like II or III of Fig. 1, or variations on them, are evidently applicable. For a case like $BCl_3 + NM_3$, curve III seems probable.[27] For $BR_3 + NR'_3$ using bulky R and R′ groups to cause steric hindrance, as in some of the work of H. C. Brown and his collaborators, curves more like II seem likely, or possibly even like I in very extreme cases.

For Group 1 D,A pairs, the terminology "outer complex" and "inner complex" can still be used, if desired, in case two minima are present in the $U(C)$ curve; but if so, it must not be assumed to have the same structural implications as for Group 3–5 pairs.

Middle Complex.—For D,A pairs in which one partner is an ion and the other a neutral closed-shell system, particularly if the donor is of the n' type, one finds $U(C)$ curves like those in Fig. 3, or variations on them. Figure 3 is applicable, for example, to D,A interactions such as

Type $n' + h\sigma_d$ (of Group 2):

$$HO^-aq + MeI \longrightarrow (HOMeI^-)aq \longrightarrow HOMe + I^-aq \quad (8)$$

Types $n' + h\sigma_a$ and $n' + x\sigma_a$:

$$\begin{aligned} F^-sl + HF &\longrightarrow (FHF)^-sl \longleftarrow FH + F^-sl \\ I^-sl + I_2 &\longrightarrow (III)^-sl \longleftarrow I_2 + I^-sl \end{aligned} \quad (9)$$

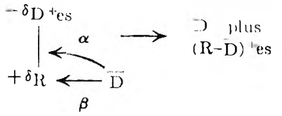
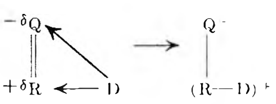
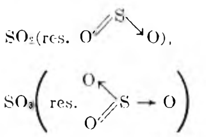
Curves I and II in Fig. 3 correspond to Group 2 cases where a reaction proceeds continuously to the right over an activation barrier or barriers near $C = 0$ (activated complex or complexes), as in the typical displacement reaction (8). Curve III is applicable in cases where association occurs giving a stable complex ion, as in (9). Here the minimum near $C = 0$ may be called a "middle complex." Reactions (9) correspond to special cases of curve III having equal values of U for numerically equal positive and negative C, and not necessarily having any activation barriers at the left and right of $C = 0$. Actually, it seems probable that there may be no such barrier for HF_2^-, at least in some solvents.

---

(27) This is supported by recent work of D. Garvin and G. B. Kistiakowsky, *J. Chem. Phys.*, 20, 105 (1952).

TABLE IV

ELECTRON ACCEPTOR (A) TYPES^a

Symbol	Name	Essential Structure	Nature of Acceptor Action^b: General Character	Nature of Acceptor Action^b: VB Description	Nature of Acceptor Action^b: MO Description	Examples	Remarks^c
v	Vacant-orbital acceptor	Neutral even system in which an orbital or orbitals of relatively high E (electron affinity) are vacant	Association for valency increase	Partial dative acceptance (cf. Eq. (1a)) of electron into vacant orbital, as follows: $D + v \longrightarrow \text{Res.}\begin{cases} D,A \\ D^+\text{—}^-v \end{cases}$	$D: + v \longrightarrow D: v$	BMe_3, $AlMe_3$, BX_3, AlX_3, FeX_3, $ZnCl_2$, $HgCl_2$, O atom, $SnCl_4$ (?), SiF_4(?)	A1, A2
v^*	Vacant-orbital cation acceptor	Even ion R^+ or usually R^+es with High-E localized orbital vacant	Same as v	Same as v	Same as v	Ag^+es, NO_2^+es, HSO_3^+es, carbonium cations Ak^+ or Ak^+es	A1, B1, B2, B3, B4
$h\sigma^*_d$ and $k\sigma^*_d$	Cationic dissociative σ acceptor	Even cation of structure DH^+es (type $h\sigma^*$), DR^+-es (type $k\sigma^*$), or in general $(D\rightarrow)_mR^{n}{}^+$es (*generalized* $k\sigma^*$ type)	Always dissociative (σ^*_d). Displacement reaction: acceptance of stronger base in place of weaker	In general, $p\bar{D} + (D\rightarrow)_mR^{n}{}^+\text{es} \rightarrow (D\rightarrow)_q(\bar{D}\rightarrow)_pR^{n}{}^+\text{es} + pD$ In particular, if acceptor is DR^+es or DH^+es,  Here D^+ and D play the same roles that Q and Q^- play in σ_d acceptor action.		$h\sigma^*_d$: H_3O^+es, NH_4^+es $k\sigma^*_d$: $Ag(NH_3)_2^+$es. Ag^+aq may also belong here, but is more conveniently regarded as v^*	B1, B2, B3, B4
$x\pi$	π acceptor	Neutral even system containing bonding π electrons relatively strongly held	$x\pi_a$ or $k\pi_a$: Loose dative association	$x\pi_a$ or $k\pi_a$: Partial acceptance of π electron by any π bonding pair, converting the latter partially into an odd π electron (which gives dative bonding to donor) plus π lone pair; with resonance of this action among all π electrons	$x\pi_a$ or $k\pi_a$: Partial acceptance of electron into lowest-energy (highest-E) antibonding π MO, with dative bonding to donor	$x\pi$: Aromatic or unsaturated hydrocarbons with electronegative or electrophilic substituents. For example, trinitrobenzene, maleic anhydride	
$k\pi$	Ketoid π acceptor	Neutral even system usually of structure Z=O (or resonating Z=O) containing strongly polar π bond(s)	$x\pi_d$ or $k\pi_d$: Association (for better saturation and electronegativity satisfaction) with the formation of one σ and the breaking of one π bond	$k\pi_d$: Partial electron acceptance by both R and Q with loss of R Q π bond and formation of R–D bond:  usually followed by rearrangements or further reaction		$k\pi$: RHCO, RR'CO, RCN, CO_2, 	C1, C2

This last statement is based on the fact that at larger C values, the attraction between F^- and HF must be a matter of (exceptionally strong) primarily electrostatic hydrogen bonding; at smaller C values, strong charge transfer binding (plus symmetrization—see Section VIII) must also set in.[28]

A viewpoint similar to that of Fig. 3 can also be used (as an alternative to Fig. 1) in certain Group 1 cases of type $n' + v$, $n + v^*$, and the like. Consider for example

$$F^-\text{sl} + BF_3 \longrightarrow BF_4^-\text{sl} \longleftarrow BF_3 + F^-\text{sl}$$

with a different F atom as F^- on the right and on the left. These reactions may be mapped as in Fig. 3 III, with $C = 0$ corresponding to BF_4^-sl. (More appropriately, there should be *four* instead of just two directions leading out from $C = 0$.) Another example is

$$NH_3 + AgNH_3^+\text{sl} \longrightarrow Ag(NH_3)_2^+\text{sl} \longleftarrow NH_3Ag^+\text{sl} + NH_3$$

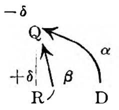
Here again Fig. 3 III might be used.

Reaction Paths and Mechanisms.—The charge transfer process idea, with the aid of Figs. 1–3, appears capable of giving plausible indications about reaction paths for a great variety of chemical reactions. In any such consideration, careful attention must be paid to the quantum-mechanical symmetry requirements of refs. 2 and 4; these requirements impose important restrictions which may prove to be valuable in deciding between otherwise plausible possibilities. In general, great CAUTION will be needed in attempting to apply the foregoing ideas to the determination of what actually may happen in specific reactions, since the possible paths, even for a single over-all reaction, are often numerous, diverse in type, and compli-

---

(28) *Cf.* G. C. Pimentel, *J. Chem. Phys.*, 19, 446 (1951), for a discussion (using non-localized MO methods) of the linear ions $(FHF)^-$ and I_3^- essentially as symmetrized charge-transfer complexes. (In I_3^-, partial trivalency of the central I atom probably also assists.) It is not certain that the free ion I_3^- is exactly linear and symmetrical; if it is not, corresponding minor modifications of obvious character are needed in curve III of Fig. 3.

TABLE IV (*Continued*)

Symbol	Name	Essential Structure	Nature of Acceptor Action[b] General Character	 VB Description	 MO Description	Examples	Remarks[c]
$x\sigma$	Halogenoid σ acceptor	Neutral even system Q_2 or $Q^\circ Q$, with usually weak σ bond between electronegative atoms or radicals	$x\sigma_a$ (also, rarely, $h\sigma_a$): loose dative association for better electronegativity satisfaction	$x\sigma_a$: $D + Q^\circ Q \rightarrow$ $\text{Res.}\left\{\begin{matrix} D,Q^\circ Q \\ (D^+{-}Q^\circ)Q^- \\ D^+Q^{\circ\,-}Q \end{matrix}\right\}$	$D + Q^\circ Q \longrightarrow$ $\text{Res.}\left\{\begin{matrix} D,Q^\circ Q \\ D^+{-}(Q^\circ Q)^- \end{matrix}\right\}$ Accepted electron in $(Q^\circ Q)^-$ goes into strongly antibonding σ MO, which gets less antibonding on dissociation	$x\sigma$: Halogen molecules X_2 and $X^\circ X$; Ph_3CH (?)	*D*
$h\sigma$ and $k\sigma$	Dissociative σ acceptors	Neutral even system HQ or RQ with usually relatively strong σ bond	$x\sigma_d$, $h\sigma_d$, or $k\sigma_d$: Dissociation, usually es-assisted, to form Q^-es	$h\sigma_d$ or $k\sigma_d$:	$D + RQ \longrightarrow$ $\text{Res.}\left\{\begin{matrix} D,RQ \\ D^+{-}RQ^- \end{matrix}\right\} \rightarrow$ (Q^- out) Accepted electron in RQ^- goes into strongly antibonding σ MO which gets less antibonding on dissociation. Partial electron acceptance by Q from both D and R (or H) with liberation of Q^- and formation of D–R bond  Q^-es plus $\xrightarrow{es}$ $(R^{1-\alpha}{-}D^{\alpha})^{+1}$es $(\beta = 1 - \alpha - \delta)$ (See eq. (5) for example with further details)	$h\sigma$: All neutral H-acids, including hydrogen halides HX water, alcohols $k\sigma$: Organic halides RX, esters	E1, E2 and E3
Q	Radical acceptor (oxidizing ing or electrophilic radical)	Odd-electron system with relatively high electron affinity				Halogen atoms, H atom, NO_2, acid radicals	

[a] See notes *a*, *b*, *c*, and *d* of Table III. [b] There appear to be two main driving forces behind acceptor action: (1) the tendency of atoms with vacant orbitals to pick up electrons to form additional bonds (valency increase); (2) the tendency of electronegative atoms in a molecule to become negatively charged (electronegativity satisfaction). The first of these is largely confined to *v* acceptors, while the second is present for most acceptors. In π-electron systems resonance effects are also important. In *all* types of acceptors acceptor strength increases on increased loading with electronegative atoms. [c] The following remarks pertain to cited cases: A1, These and v^* are *the* typical Lewis acids; A2, really the vacant orbital is not quite vacant, because of resonance structures like $\begin{matrix}X\\ \\ X\end{matrix}\!\!>\!B^-{=}X^+$ or $Cl^+{=}Hg^={=}Cl^+$, and to this extent *v* acceptors are $k\pi$ acceptors like RR′C=O and O=C=O; B1, The v^* acceptors are typical Lewis acids. Luder calls the σ^* acceptors secondary Lewis acids; B2, Ions of structure R^+sl are classified as v^* or as $k\sigma^*$ according as the solvent molecules (sl) are held primarily by es or by donor action and so regarded as accessory or as constitutive. In doubtful cases, the v^* classification is the more convenient. Ions of structure H^+sl are almost always most properly called $h\sigma^*$ rather than v^*; B3, However even definitely $k\sigma^*$ or $h\sigma^*$ acceptors are often conveniently regarded *by courtesy* as v^*, by ignoring sl in R^+sl or H^+sl; for example, H_3O^+aq may be regarded as H^+; B4, The type $h\sigma^*$ comprises precisely the conjugate acids DH^+ of all neutral bases D. Examples include among others ArH^+ and UnH^+. However, since UnH^+ is at the same time R^+ (*e.g.*, if Un is C_2H_4, UnH^+ is $C_2H_5{}^+$), acceptors of this type function more often associatively as v^* acceptors in their own right than dissociatively as $h\sigma^*{}_d$ acceptors; C1, $k\pi$: The $k\pi$ and *v* acceptors are not separated by any sharp boundary, but a continuous range of intermediate cases is possible (see remark A2 on *v* acceptors); C2, Some readers may question the structural formulations given here for SO_2 and SO_3, but it is the writer's considered opinion that they correspond to the major resonance components, and that, for instance, structures using *d* orbitals to give hexavalent sulfur with more double bonds are present only to a lesser extent; D, $x\sigma$: The halogen molecules X_2 and $X^\circ X$ are characterized by (a) weak σ bonds, (b) $E^{vert} > 0$ though small, but increasing strongly during dissociation to limiting value E_X; E1, The $h\sigma$ class consists precisely of all the neutral H-acids; E2, The halides HX and RX are characterized by (a) strong polar σ bonds, (b) $E^{vert} \ll 0$, but becoming > 0 during dissociation, with limiting value E_X; E3, HQ and RQ are sometimes described as secondary Lewis acids, conceived as formed from the primary Lewis acid H^+ or R^+ and the base Q^-.

cated, and dependent on temperature, pressure, the nature of the medium, and other factors.

X. Corrections and Improvements on Previous Papers

Some improvements in the donor and acceptor classes and classification symbols of paper II[2] are described in Section II above. An error in quoting spectroscopic data on $Et_2O{\cdot}I_2$ in paper I[4] is corrected in Table VI (reaction-type 13, footnote *v*). A revision of Fig. 5 of paper II is described in Table VI (reaction-type 7, footnote *m*). An overlooked reference of some importance relevant to paper I is: Childs and Walker, *Trans. Faraday Soc.*, **34**, 1506 (1938), on the spectra of bromine in benzene, acetic acid, water and ethyl alcohol.

In paper I, on page 606, two pairs of resonance structures given for $R'RO{\cdot}I_2$, and called (I) and (II), are not independent; pair (II) should be

TABLE V: NATURE OF PRODUCTS IN SOME DONOR-ACCEPTOR REACTIONS[a]

Acceptor Type	Donor Type n	n' (usually Q^-es)	$b\pi$ $b\pi_a$	 $b\pi_d$	$b\sigma$ (commonly RQ) $b\sigma_a$	 $b\sigma_d$	R $\{R_n, R_\pi, R_\sigma\}$
v	DATIVE (1)	<Sy>-DATIVE (2)	Dative (3)			es: $R^+[Qv]^-es$ (4)	
v^* (Usually R^+es)	<Sy>-DATIVE (5)	DATIVE forming RQ; or Sy-DATIVE (6)	Dative (7)	($b\pi$)–R σ-bond formed datively, with loss of one π bond (7)		$R^+{}_Des + QR_A$ (8)	(25)
π $x\pi\begin{cases}x\pi_a\\x\pi_d\end{cases}$	Dative (9) Q–($x\pi$) σ-bond formed datively, with loss of one π-bond (10)		Dative (11)				
$k\pi$ (usually Z=O) $\begin{cases}k\pi_a\\k\pi_d\end{cases}$	Dative (9) <es>: n^+–Z–O^- → (9)	es-dative (10) Q–Z–O^-es <→> (10)	Dative (11)			(12)	
σ $x\sigma$ ($Q^\circ Q$) $\begin{cases}x\sigma_a\\x\sigma_d\end{cases}$	Dative (13) es: $[nQ^\circ]^+Q^-es$ <→> (13) es,v: $[nQ^\circ]^+[vQ]^-es$ <→>	Sy-dative (16)	Dative (18)	es: $[\pi Q^\circ]^+Q^-es$ <→> es,v: $[\pi Q^\circ]^+[vQ]^-es$ <→> (18)	Dative (20)		
$h\sigma$ (HQ) $\begin{cases}h\sigma_a\\h\sigma_d\end{cases}$	Unstable or H-bonded (14) es: $[nH]^+Q^-es$ (14)	Sy-dative (16) $Q_DH + Q^-{}_Aes$ (17)	H-Bonded (19)	es: $[\pi H]^+Q^-es$ (19) es,v: $[\pi H]^+[vQ]^-es$ (19)]		$(Q_DHQ_A)^- + R^+$ (21) $h\sigma_d$: Perhaps es: $Q_DH + R^+Q^-{}_Aes$ (21)	$R^+Q^- + H$
$k\sigma$ (RQ) $\begin{cases}k\sigma_a\\k\sigma_d\end{cases}$	Unstable (14) es: $[nR]^+Q^-es$ (14)	$Q_DR + Q^-{}_Aes$ (17)	$k\sigma_a$: Unstable or H-bonded (19)				$R^+{}_DQ^- + R_A$ (25)
$l\sigma_d(n^\circ v)$	$nv + n^\circ$ (15)						
σ^* $x\sigma^*{}_d$ ($[Q^\circ D]^+es$)							
$h\sigma^*{}_d$ ($[HD]^+es$)	$[nH]^+es + D$ (22)	QH + D (23)				Perhaps $QH + R^+es + D$ (24)	
$k\sigma^*{}_d$ ($[RD]^+es$)	$[nR]^+es + D$	QR + D (23)					
$Q\{Q_v, Q_\pi, Q_\sigma\}$		(25)	Dative (25)				RQ or R^+Q^- (25)

[a] For detailed descriptions of donor (D) and acceptor (A) types and notation, see Tables III and IV. Subscripts a and d appended to donor and acceptor symbols of the σ and π classes indicate associative (a) or dissociative (d) functioning. For any donor–acceptor type, Table V describes briefly the nature of the initial reaction-product or products for a direct bimolecular reaction between donor and acceptor. The word "dative" indicates a *loose* dative complex, the word "DATIVE" a dative complex or compound which in typical examples is strongly bound. The *numbers in parentheses* in Table V refer to Sections of Table VI where specific examples of the reaction-types indicated are listed.

In Table V, certain symbols and punctuation marks are used only with definite explicit meanings, as follows: parentheses are used with a brief structural description of a donor or acceptor type; <. . .> means that the indicated behavior *may* or *may not* occur in a given example depending on circumstances, and/or that it occurs in some examples but not in all; → means that an indicated reaction product is an intermediate (stable or unstable) which normally reacts further (either intramolecularly and/or, usually, with other molecules). *Subscripts* D and A serve, when necessary, to identify different R and/or Q radicals in the reaction-products in terms of their origin in the donor or acceptor reactant. The abbreviation es or es,v followed by a colon indicates that the reaction occurs conditionally (in most cases, only conditionally)—see Section VI—through coöperative action of agents acting electrostatically (es), or through the coöperation of an auxiliary v acceptor plus es agents (es,v). The symbol Sy, standing for symmetrization, denotes a process in which, when an incoming donor or acceptor joins a partner containing identical (or sufficiently similar) atoms, all the like atoms become mutually equivalent (or nearly so) in position and internal electronic distribution (see Section VIII).

Tables V and VI are not exhaustive: (a) additional D and A types exist, *e.g.*, n'' and σ' donors, v^{**}, v^{***} and π^* acceptors, etc.; (b) additional reaction-types corresponding to some of the blanks in Table V exist, but only those types are listed in Table V of which examples are given in Table VI; (c) reaction-types involving R donors and Q acceptors are indicated only very sketchily. Tables V and VI are *not intended to imply that the actual reaction mechanism* for a given donor and acceptor is necessarily always (or perhaps ever) the direct bimolecular mechanism indicated in the tables. However, the reaction-types listed are believed to be correct at least as to over-all driving force and over-all result, although whether for any given individual example they go at all, or reach an equilibrium, or go to completion, depends of course on the acceptor and donor strengths of the particular reactants. The reaction-types listed are believed also to correspond in most cases to reaction mechanisms which are likely to be realized in practice at least under some circumstances. As is well known, over-all bimolecular reactions often proceed actually in steps, with the monomolecular or quasi-monomolecular ionization process $RQ \rightarrow R^+sl + Q^-sl$ as an initial step, the solvent (sl) action involved being sometimes purely electrostatic (es) and sometimes partly or wholly a donor or acceptor action. The v^* or $\sigma^*{}_d$ acceptor R^+sl and/or the n' or $\sigma'{}_d$ donor ($\sigma'{}_d$ is of structure $n'v$) then react further. (The ionization process is the reversal of a donor-acceptor reaction of type v^* or $\sigma^*{}_d$ plus n' or $\sigma'{}_d \rightarrow RQ$.) In a few examples in Tables V and VI, processes involving the assistance of an auxiliary acceptor or donor (usually a v acceptor) have been indicated. No opinion is implied here as to whether ever, or how often, the actual reaction mechanism in such processes is termolecular.

dropped. Resonance between the two equivalent forms (I) gives I_2^- 3-electron bonding *together* with O^+–I electron-pair bonding, the two effects being nearly but not quite additive so long as the O^+–I bonding is weak.

Acknowledgment.—The writer is indebted to various people for helpful suggestions and criticisms, and particularly to Dr. Harden McConnell.

Appendix

Detailed Characterization of Donor and Acceptor Classes and Their Interaction Types, with Examples

TABLE VI

SOME EXAMPLES OF DONOR–ACCEPTOR COMPLEXES (D·A), COMPOUNDS (D→A), AND PROBABLE REACTIONS (D + A → PRODUCTS), MOSTLY IN SOLUTION, TOGETHER WITH APPROXIMATE WAVE LENGTHS λ OF PROBABLE CHARGE TRANSFER ABSORPTION SPECTRA PEAKS OF SOME OF THE COMPLEXES D·A[a,b,c]

1, Type $n + v$[d]

$Et_2O + BF_3 \longrightarrow Et_2O{\to}BF_3$
$Me_3N + BMe_3 \longrightarrow Me_3N{\to}BMe_3$
$Me_3N + {}^1/_2Al_2Cl_6 \longrightarrow Me_3N{\to}AlCl_3$
$MeCN + BF_3 \longrightarrow MeCN{\to}BF_3$
$MeBr + {}^1/_2Ga_2Cl_6 \longrightarrow MeBr{\to}GaCl_3$[e]
But *not* $HCl + AlCl_3 \longrightarrow HCl{\to}AlCl_3$[f]
$Me_3P{\to}O + BF_3 \longrightarrow Me_3P{\to}O{\to}BF_3$[g]
$Me_3N{\to}O$; Res. $OS{\to}O$; Res. $O_2S{\to}O$

2, Type $n' + v$ (usually Q^-es + v)

$F^-aq + BF_3 \longrightarrow BF_4^-aq$
$HO^-aq + BF_3 \longrightarrow HOBF_3^-aq$
$Na^+Cl^-(\text{solid}) + AlCl_3 \longrightarrow Na^+AlCl_4^-(\text{solid})$

3, Type $b\pi + v$

$b\pi_a$: Complexes of the type $b\pi_a{\cdot}v$ are not very stable[h]

4, Type $b\sigma + v$

$b\sigma_d$: $RF + BF_3 \longrightarrow R^+es + BF_4^-es$ or $R^+BF_4^-$ (R = alkyl) in RF as es solvent

$NOCl + AlCl_3 \longrightarrow NO^+AlCl_4^-(\text{solid}) \rightleftarrows NO^+sl + AlCl_4^-sl$, *e.g.*, in liquid NOCl[i]

$COCl_2 + AlCl_3 \longrightarrow COCl^+sl + AlCl_4^-sl$, *e.g.*, in liquid $COCl_2$

For reactions like the above, direct reaction and initial ionization of the solvent are alternative mechanisms, either of which may be predominant depending on the particular case and circumstances.

5, Type $n + v^*$

$CH_2I_2 + Ag^+aq \rightleftarrows CH_2I_2{\cdot}Ag^+aq$[j]

(here perhaps Ag^+aq is more nearly of $k\sigma^*_d$ than v^* type)

$Me_3N + Me^+es \longrightarrow Me_4N^+es$

(perhaps in MeF solution, after $MeF + BF_3 \longrightarrow Me^+es + BF_4^-es$)

$2NH_3 + Ag^+NO_3^-(\text{crystal}) \xrightarrow{es} (H_3N{\to})_2Ag^+es + NO_3^-es$

(in aq or aqueous ammonia, with aq as es)

6, Type $n' + v^*$[d]

$Cl^-sl + Ph_3C^+sl \rightleftarrows Ph_3CCl$[k]

in liquid SO_2, nitromethane, or acetone (sl action in Cl^-sl partly dative: see under $n' + k\pi$ (Part 10 of this Table))

$I^-aq + Ag^+aq \longrightarrow AgI(\text{solid}) + aq$

(see remarks on Ag^+aq under $n + v^*$ (Part 5 of this Table))

$2CN^-aq + Ag^+aq \longrightarrow [Ag(CN)_2]^-aq$

7, Type $b\pi + v^*$

$b\pi_a$: $Bz + Ag^+ClO_4^- \rightleftarrows Bz{\cdot}Ag^+ClO_4^-$, and $(Bz{\cdot}Ag^+{\cdot}Bz)ClO_4^-$?

(in benzene solution)

$MePh + Ag^+aq \rightleftarrows MePh{\cdot}Ag^+aq$ (λ2300?)[m] and $aqAg^+{\cdot}MePh{\cdot}Ag^+aq$

(in aqueous solution; here see remark on Ag^+aq under $n + v^*$ (Part 5 of this Table))

$b\pi_d$: $Bz + NO_2^+es + HSO_4^-es \longrightarrow [BzNO_2]^+es + HSO_4^-es \longrightarrow PhNO_2 + H_2SO_4$

(in sulfuric acid solution, with sulfuric acid as es)

$Bz + R^+es + AlCl_4^-es \longrightarrow [BzR]^+es + AlCl_4^-es \longrightarrow PhR + HCl + AlCl_3$ (?)

(*e.g.*, perhaps EtCl solution of $AlCl_3$ ($\longrightarrow Et^+es + AlCl_4^-es$) + Bz)[h]

8, Type $b\sigma + v^*$

$b\sigma_d$: $MeEt_2CH + Me_2CH^+ \longrightarrow MeEt_2C^+ + Me_2CH_2$[n]

(Here in the $b\sigma_d$ donor RQ, R is $MeEt_2C$, Q is H)

$Zn\ \text{metal} + Ag^+sl \longrightarrow Zn^{++}sl + Ag\ \text{metal}$

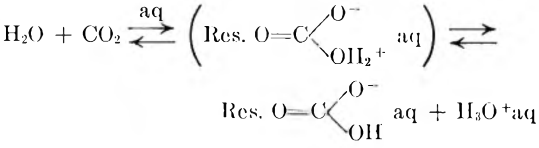
$Na\ \text{metal} + NH_4^+sl \longrightarrow Na^+sl + Na(\text{metal})\text{—}NH_4$ which decomposes to give NH_3 and H_2

9, Types $n + x\pi$ **and** $n + k\pi$

$x\pi_a$: $NH_3 + \text{dinitrobenzene} \rightleftarrows NH_3{\cdot}\text{dinitrobenzene}$

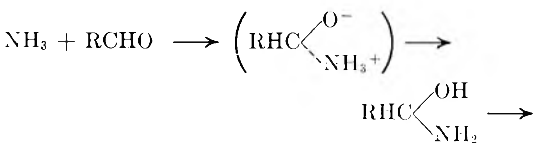
$k\pi_a$: $Me_3N{\to}O + SO_2 \longrightarrow Me_3N{\to}O{\to}SO_2$[e]

$k\pi_d$:



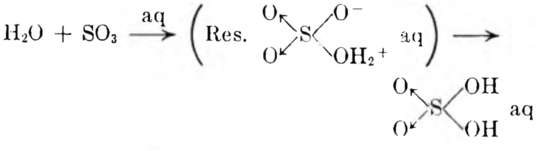
$$H_2O + CO_2 \overset{aq}{\rightleftarrows} \left(\text{Res. } O{=}C\begin{matrix}O^-\\ OH_2^+\end{matrix}\ aq\right) \rightleftarrows \text{Res. } O{=}C\begin{matrix}O^-\\ OH\end{matrix}\ aq + H_3O^+aq$$

(or perhaps $CO(OH)_2$ is formed in the first step)



$$NH_3 + RCHO \longrightarrow \left(RHC\begin{matrix}O^-\\ NH_3^+\end{matrix}\right) \longrightarrow RHC\begin{matrix}OH\\ NH_2\end{matrix} \longrightarrow$$

(In this and the first following, or probably both the following, examples, the over-all process is of the type $b\sigma_d + k\pi_d$, with an *intramolecular* $b\sigma_d$ action. If the action proceeds in a *single step*, it should be classified as $b\sigma_d + k\pi_d$.)



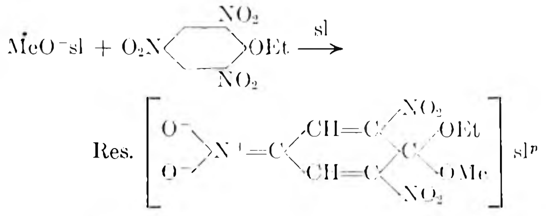
$$H_2O + SO_3 \xrightarrow{aq} \left(\text{Res. } \begin{matrix}O\nwarrow\\ O\swarrow\end{matrix}S\begin{matrix}O^-\\ OH_2^+\end{matrix}\ aq\right) \longrightarrow \begin{matrix}O\nwarrow\\ O\swarrow\end{matrix}S\begin{matrix}OH\\ OH\end{matrix}\ aq$$

$HCl + SO_3 \longrightarrow HCl{\to}SO_3$ or $ClSO_2OH$ (?) (chlorsulfonic acid)[o]

TABLE VI (*Continued*)

10, Types $n' + x\pi$ *and* $n' + k\pi$

$x\pi_d$:



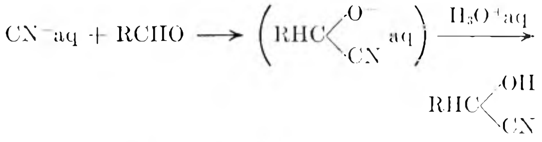
(in solution, with sl = es)

$k\pi_a$: $(Cl^-\cdot SO_2)sl$ or $(Cl^-\rightarrow SO_2)sl$

(sl action on Cl^- partly es, partly dative)

$(Cl^-\cdot CH_3NO_2)sl$ and $(Cl^-\cdot Me_2CO)sl$ in nitromethane and acetone

$k\pi_d$:



$$CN^-aq + RCHO \longrightarrow \left(RHC\begin{smallmatrix}O^-\\ CN\end{smallmatrix}\ aq\right) \xrightarrow{H_3O^+aq} RHC\begin{smallmatrix}OH\\ CN\end{smallmatrix}$$

$OH^-aq + CO_2 \longrightarrow HCO_3^-aq$

Na^+Cl^- (solid) + $SO_3 \longrightarrow Na^+[ClSO_3]^-$ (solid)

11, Types $b\pi + x\pi$ and $b\pi + k\pi$[a]

$b\pi_a\cdot x\pi_a$: $PhNH_2$ + s-trinitrobenzene $\rightleftarrows$ $PhNH_2$·s-trinitrobenzene (λ 4000)[q]

Bz + s-trinitrobenzene $\rightleftarrows$ Bz·s-trinitrobenzene (λ 2800)[r]

$b\pi_a\cdot k\pi_a$: MBz + SO_2 $\rightleftarrows$ MBz·SO_2 (λ 2840)[s]

(MBz = various methylated benzenes)

Bz + oxalyl chloride $\rightleftarrows$ Bz·oxalyl chloride (λ 2700?)[t]

Hydroquinone + quinone $\rightleftarrows$ hydroquinone·quinone (quinhydrone) (about λ 5600 in crystal)[u]

12, Type $b\sigma_d + k\pi_d$

(see under $n + k\pi$, Part 9)

13, Type $n + x\sigma$

$x\sigma_a$: t-butyl alcohol + I_2 $\rightleftarrows$ t-Bu alcohol·I_2 (λ 2330)[v]

$Et_2O + I_2 \rightleftarrows Et_2O\cdot I_2$ (λ 2480)[v]

$RX + X_2 \longrightarrow RX\cdot X_2$ (λ 3000–3500)[v,a] (X = Br or I)

$x\sigma_a$ and $x\sigma_d$: $Py + I_2 \rightleftarrows Py\cdot I_2 \underset{}{\overset{slow}{\rightleftarrows}} [PyI]^+py + I^-py$; etc.[w]

(In pyridine solution. In $Py\cdot I_2$, Py may be acting as a *mixed n* and $b\pi_n$ donor.)

$H_2O + I_2 \rightleftarrows H_2O\cdot I_2 \overset{aq}{\rightleftarrows} [H_2OI]^+aq + I^-aq \overset{H_2O}{\rightleftarrows} HOI + H_3O^+aq + I^-aq$ (and $I^-aq + I_2 \rightleftarrows I_3^-aq$, etc.)

$NH_3 + I_2 \rightleftarrows H_3N\cdot I_2 \overset{aq\ am}{\rightleftarrows} [H_3NI]^+es + I^-es \rightleftarrows NH_2I + NH_4^+es + I^-es$[x]

14, Types $n + h\sigma$ and $n + k\sigma$[d,y]

$n\cdot h\sigma_a$ and $n\cdot k\sigma_a$: Theoretically, since almost certainly $E^{vert} << 0$ for HX (X = halogen) and probably for most HQ and RQ, it is probable that any loose complexes of the type $n\cdot h\sigma_a$ and $n\cdot k\sigma_a$ which may exist are in most cases due to electrostatic rather than charge transfer forces (*cf.* Sections VI, IX). Formation of onium acids or salts ($k\sigma_d$ or $k\sigma_d$ behavior) usually (if not always) occurs only with es assistance ($h\sigma_{ed}$ or $k\sigma_{ed}$ behavior), either by formation of an ionic crystal or by solvation. For example, $NH_4^+Cl^-$ solid, and $NH_4^+sl - Cl^-sl$, are stable, but individual $NH_4^+Cl^-$ molecules in vapor (*cf.* refs. 23 and 24 and Section IX) or in inert solvents are apparently not stable (nor apparently is a loose complex $NH_3\cdot HCl$ very stable). It may be, however, that individual salt molecules are in *some* cases stable without es assistance; for example, perhaps $Me_4N^+Cl^-$ and the like in benzene solution.

$h\sigma_d$: $H_2O + HCl \xrightarrow{aq} H_3O^+es + Cl^-es$ (es = aq)

$H_2O + HBr \xrightarrow{SO_2} H_3O^+es + Cl^-\cdot SO_2$ (es = SO_2)

$H_3N + HOH \overset{aq}{\rightleftarrows} NH_4^+es + OH^-es$ (es = aq)

$k\sigma_d$: $Me_3N + MeCl \xrightarrow{slow} [Me_4N]^+Cl^-$ (slightly soluble solid)

(in Bz or $PhNO_2$ solution)

15, Type $n + l\sigma$[d]

$l\sigma_d$: $Me_2CO\rightarrow BCl_3 + Py \longrightarrow Py\rightarrow BCl_3 + Me_2CO$

15, Types $n' + x\sigma_a$ and $n' + h\sigma_a$

$x\sigma_a$: $I^-aq + I_2 \rightleftarrows I_3^-aq$

$h\sigma_a$: $F^-aq + HF \longrightarrow HF_2^-aq$ (*cf.* also $b\sigma + h\sigma$ below (Part 21) concerning HCl_2^-)

17, Types $n' + h\sigma_d$ and $n' + k\sigma_d$[b]

$h\sigma_d$: $NH_2^-es + HCPh_3 \longrightarrow NH_3 + CPh_3^-es$

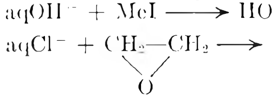
(in liquid ammonia solution)

$EtO^-es + HCH_2COOEt \rightleftarrows EtOH + [CH_2COOEt]^-es$

(in EtOH solution)

$k\sigma_d$: $aqI^- + MeI \longrightarrow IMe + I^-aq$

$aqOH^- + MeI \xrightarrow{slow} HOMe + I^-aq$



$$aqCl^- + \underset{O}{CH_2\!-\!CH_2} \longrightarrow$$

$Cl-CH_2-CH_2-O^-aq + HOH \longrightarrow Cl-CH_2-CH_2-OH + OH^-aq$

This example is of the type

$(n') + (k\sigma_d) \longrightarrow (n') + (h\sigma_d) \longrightarrow$ etc.

18, Type $b\pi + x\sigma$

$b\pi_a\cdot x\sigma_a$: $MBz + X°X \rightleftarrows MBz\cdot X°X$ (λ 2900)[y,a]

(MBz = various methylated benzenes, X°X = Cl_2, Br_2, I_2, ICl)

Naphthalene + $X_2 \rightleftarrows$ naphthalene·X_2 (λ 3500)[y,b]

$MC_2H_4 + I_2 \rightleftarrows MC_2H_4\cdot I_2$ (λ 2700–3000)[z]

(MC_2H_4 = various methylated ethylenes)

$Bz + Ph_3CH \longrightarrow Bz\cdot Ph_3CH$[a]

TABLE VI (*Continued*)

$b\pi_d + x\sigma_d$: $\mathrm{Bz + Cl_2 + FeCl_3 \longrightarrow ([BzCl]^+[FeCl_4]^-) \longrightarrow PhCl + HCl + FeCl_3 \longrightarrow}$

$\mathrm{C_2R_4 + Cl_2 + AlCl_3 \longrightarrow ([C_2R_4Cl]^+[AlCl_4]^-)}$

(double charge transfer reactions of type $b\pi_d + x\sigma_d + v$)

19, Types $b\pi + h\sigma$ and $b\pi + k\sigma$

$b\pi_a \cdot h\sigma_a$: There is evidence for loose complexes of the types $b\pi_a \cdot h\sigma_a$ (*e. g.*, methylated benzenes with HCl)[aa] and $b\pi_a \cdot k\sigma_a$ (*e.g.*, Bz·MeOH).[ab] These, however, are almost certainly members of a large class of weakly H-bonded es complexes,[ac] and not dative complexes. Presumably the H of MeOH or of HCl is attracted by the somewhat negatively charged carbons of the benzene ring (the C–H bonds are believed to have polarity $\mathrm{C^-H^+}$). This would explain the increasing solubility with increasing methylation observed by Brown and Brady[aa] for HCl in MBz, since increasing methylation sends negative charge increasingly into the ring. Brown and Brady attribute the effect to increasing basicity, which would indeed give the same result, and which (interpreting basicity as meaning charge transfer donor strength) is indeed here believed responsible for the increasing stability with methylation of the superficially closely analogous $\mathrm{MBz + X_2}$ complexes of type $b\pi_a \cdot x\sigma_a$; but it appears improbable that charge transfer donor–acceptor interaction is appreciable for typical $h\sigma$ and $k\sigma$ acceptors without es solvent assistance (see remarks above under Types $n + h\sigma$ and $n + k\sigma$, Part 14).

$b\pi_d, h\sigma_d$: $\mathrm{C_2R_4 + HHSO_4 \overset{es}{\rightleftarrows} [C_2R_4H]^+es + HSO_4^-es}$

(in sulfuric acid as es)

$\mathrm{Ar + HF \overset{HF}{\rightleftarrows} [ArH]^+es + F^-es\ [or\ HF_2^-es)}$[ad]

$\mathrm{Ar + HF + BF_3 \rightleftarrows [ArH]^+es + BF_4^-es}$

(in liquid HF as es)[ae]

$\mathrm{PhMe + HCl + {}^1/_2Al_2Cl_6 \rightleftarrows [MePhH]^+[AlCl_4]^-}$ etc.

(in toluene solution at low temperatures)[af]

20, Type $b\sigma + x\sigma$

$b\sigma_a \cdot x\sigma_a$: $\mathrm{Cyclopropane + I_2 \rightleftarrows cyclopropane \cdot I_2}$ (λ 2400)[z]

21, Types $b\sigma + h\sigma$ and $b\sigma + k\sigma$

$b\sigma_d, h\sigma_a$: anisyl chloride + HCl $\longrightarrow$ (anisyl)$^+$ + $\mathrm{HCl_2^-}$ (?)

(in liquid HCl)[b]

$b\sigma_d, h\sigma_d$: possibly (?) $\mathrm{NO_2OH + HHSO_4 \xrightarrow{es} NO_2^+es + HSO_4^-es + H_2O}$

(in sulfuric acid as es)

22, Type $n + h\sigma^*$

$h\sigma_d^*$: $\mathrm{R_3N + H_3O^+aq \longrightarrow [R_3NH]^+ + H_2O}$

$\mathrm{H_2O + [H_2OI]^+aq \longrightarrow H_3O^+aq + HOI}$ (*cf.* Type $n + x\sigma$, Part 13)

23, Types $n' + h\sigma^*$ and $n' + k\sigma^*$

$h\sigma_d^*$: $\mathrm{MeCOO^-aq + H_3O^+aq \longrightarrow MeCOOH + H_2O}$

$k\sigma_d^*$: $\mathrm{OH^-aq + Me_3S^+aq \longrightarrow MeOH + Me_2S}$

24, Type $b\sigma_d + k\sigma^*_d$

$\mathrm{Ca\ metal + COCl^+sl \longrightarrow CO}$ (from metal—CO?) $\mathrm{+ Ca^{++}sl + Cl^-sl}$

(in $\mathrm{COCl_2}$ solution)

25, Some Types Involving R or Q

$R_n + v^*$: $\mathrm{H + H^+ \xrightarrow{sy} H_2^+}$ (in gas)

$R_n + k\sigma_d$: $\mathrm{Na + MeCl \longrightarrow Na^+Cl^- + Me}$ (in gas)

$n' + Q_v$: $\mathrm{Cl^- + Cl \xrightarrow{sy} Cl_2^-}$ (in gas)

$b\pi_a + Q_\sigma$: $\mathrm{MBz + Ph_3C \longrightarrow MBz \cdot Ph_3C}$

(MBz = methylated benzenes)

$R_n + Q_v$: $\mathrm{Na + Cl \longrightarrow Na^+Cl^-}$ (near λ 3000)[ag]

$R_n + R_n$: $\mathrm{H + H \longrightarrow H_2}$ (λ 1010)[ah]

$Q_v + Q_v$: $\mathrm{I + I \longrightarrow I_2}$ (λ 1800)[ah]

$R_n + Q_v$: $\mathrm{H + I \longrightarrow HI}$ (est. λ 1280)[ah]

(These last four examples illustrate *inter-atomic* charge transfer spectra.)

[a] For numerous examples of organic and organic–inorganic molecular complexes and compounds, mostly in the solid state, see P. Pfeiffer, "Organische Molekülverbindungen," 2nd edition, F. Enke, Stuttgart, 1927. [b] For references and discussion of a great many examples of donor–acceptor reactions and their mechanisms see L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N.Y., 1940. For additional examples, see Luder and Zuffanti, ref. 6. [c] The expression "Res." means a mixture of equivalent structures of the type given. The dative bond arrow symbol, as in D→A, represents not a *pure* dative structure but a resonance mixture of pure dative structure with some no-bond structure (*cf.* Eq. (1a)). [d] W. F. Luder (*J. Chem. Phys.*, **20**, 525 (1952)) describes on the one hand the 1:1 reaction types $n' + v^*$ and $n + v$ as neutralization processes (*e.g.*, $\mathrm{CN^- + H^+ \rightarrow HCN}$ and $\mathrm{Me_2CO + BCl_3 \rightarrow Me_2CO{\rightarrow}BCl_3}$) and on the other hand the types $n + h\sigma_d$ and $n + l\sigma_d$ (*e.g.*, $\mathrm{HOH + HCN \rightarrow H_3O^+ + CN^-}$ and $\mathrm{Py + Me_2COBCl_3 \rightarrow PyBCl_3 + Me_2CO}$) as displacement processes, with $\mathrm{H^+}$ and $\mathrm{BCl_3}$ in the first pair regarded as primary Lewis acids, HCN and $\mathrm{Me_2COBCl_3}$ in the second pair as secondary Lewis acids (*cf.* Section I for related comments). [e] H. C. Brown, H. Pearsall and H. P. Eddy, *J. Am. Chem. Soc.*, **72**, 5347 (1950). [f] *Ibid.*, and H. C. Brown and H. Pearsall, *ibid.*, **73**, 4681 (1951); R. L. Richardson and S. W. Benson, *ibid.*, **73**, 5096 (1951). [g] A. B. Burg and W. E. McKee, *ibid.*, **73**, 4590 (1951). [h] Regarding $\mathrm{Ar \cdot AlX_3}$, see R. E. Van Dyke, *ibid.*, **72**, 3619 (1950); D. D. Eley and P. J. King, *Trans. Faraday Soc.*, **47**, 1287 (1951). H. C. Brown and W. J. Wallace have found $\mathrm{Bz \cdot Al_2Br_6}$ (private communication). [i] A. B. Burg and D. E. McKenzie, *J. Am. Chem. Soc.*, **74**, 3143 (1952). [j] L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 5733 (1951). [k] *Cf.* N. N. Lichtin and P. D. Bartlett, *ibid.*, **73**, 5530 (1951). [m] R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 640 (1952). For the toluene·Ag$^+$aq complex, Keefer, and Andrews' analysis shows (1) an absorption peak near λ 2650, of about double the intensity and at slightly longer wave lengths than a corresponding peak of toluene by itself; (2) rapidly rising intensity at shorter wave lengths toward a much more intense peak (not reached) which might lie at about λ 2300. This second absorption is here tentatively identified as the charge-transfer (toluene→Ag$^+$) absorption. (Ag$^+$aq also shows a strong peak at somewhat shorter wave lengths, which may tentatively be identified with $\mathrm{H_2O{\rightarrow}Ag^+}$ charge transfer.)

In ref. 2, Fig. 5 suggests that the (toluene→Ag$^+$) charge transfer peak might be expected near λ 3100. However, in constructing Fig. 5, previously existing estimates of the solvation energy of Ag$^+$ (see for example O. K. Rice, "Electronic Structure and Chemical Binding," McGraw–Hill Book Co., Inc., New York, N. Y., 1940: on p. 402 the solvation energy of Ag$^+$ in water is given as 106 kcal./mole) were overlooked. Making use of these, curve E of Fig. 5 would be raised by 1 or 2 ev. (perhaps by 2 ev. at

TABLE VI (*Continued*)

large *R* and 1 ev. at small *R*), and could very well be consistent with a charge transfer peak near λ 2300.

For an important recent survey on Ag^+ complexes, see G. Salomon, in the book, "Proceedings of Symposium on Cationic Polymerization and Related Complexes," edited by P. H. Plesch (Cambridge, 1952).

[n] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Am. Chem. Soc.*, 66, 1531 (1944). [o] *Cf.* H. H. Sisler and L. F. Audrieth, *ibid.*, 61, 3392 (1939), for references and studies on this and related examples. [p] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, N. Y., 1941, p. 481. [q] J. Landauer and H. McConnell, *J. Am. Chem. Soc.*, **74**, 1221 (1952). And see ref. 15 in text of Section III, above. [r] H. McConnell and D. M. G. Lawrey, submitted to *J. Am. Chem. Soc.* [s] L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 4169 (1951). [t] B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, 19, 994 (1951). [u] See K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952), on polarized light spectra of this and other $b\pi_a \cdot k\pi_a$ complexes in solid state. (See text, Section IV, for further details.) [v] Regarding $Et_2O \cdot I_2$, *cf.* refs. 4 and 2 in text. In the first reference (p. 606), ϵ_{max} for the λ2480 peak was in error; it should be about 7760. Confirmed by recent work by J. S. Ham, extended also to (*t*-butyl alcohol)$\cdot I_2$ (see text, Section IV). [va] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **74**, 1891 (1952). [w] L. F. Audrieth and E. J. Birr, *ibid.*, **55**, 668 (1933); R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951). See also ref. 2 in text. [x] R. K. McAlpine, *J. Am. Chem. Soc.*, **74**, 725 (1952). [y] See also Section IX of text. [ya] *Cf.* refs. 4, 2, in text. [yb] Blake, Winston and Patterson, *J. Am. Chem. Soc.*, **73**, 4437 (1951). [z] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 458 (1952); S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952). Various substituted ethylenes and butadienes, also (F and S) cyclopropane$\cdot I_2$. [aa] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **71**, 3573 (1949); **74**, 3570 (1952); solubilities of HCl in methylated benzenes. However, E. K. Plyler and D. Williams (*Phys. Rev.*, **49**, 215 (1936)) found but little shift in the HCl infrared fundamental for benzene solutions as compared with HCl vapor, whereas for other solvents (*e.g.*, nitrobenzene, ethers) large shifts were found: W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939). [ab] L. H. Jones and R. M. Badger, *J. Am. Chem. Soc.*, **73**, 3132 (1951). [ac] Work by many authors. Some recent papers including key references to earlier papers are: S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951), and references on infrared spectra in footnotes *aa* and *ab*. [ad] Klatt, *Z. anorg. allegem. Chem.*, **234**, 189 (1937); M. Kilpatrick, unpublished work. [ae] D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951). M. Kilpatrick, unpublished work. [af] H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.*, **74**, 191 (1952). [ag] *Cf.* R. S. Mulliken, *Phys. Rev.*, **51**, 327 (1927). [ah] *Cf.* R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics* (London Physical Society), **8**, 249 (1941).

DISCUSSION

H. C. **BROWN**.—From a chemical viewpoint the interactions of iodine and hydrogen chloride with various types of donor molecules exhibit close similarity. Thus, both substances interact with aromatic nuclei to form relatively unstable 1:1 complexes.

$$ArH + I_2 \rightleftarrows ArH \cdots I{-}I$$

$$ArH + HCl \rightleftarrows ArH \cdots H{-}Cl$$

With somewhat stronger bases, such as ethyl ether, they interact to form stabler 1:1 complexes.

$$R_2O + I_2 \rightleftarrows R_2O{-}I{-}I$$

$$R_2O + HCl \rightleftarrows R_2O{-}H{-}Cl$$

Although there is stronger bonding between the two components, and the bonds between the iodine atoms and between hydrogen and chlorine must be correspondingly weakened, the situation has evidently not reached the point where the halide ion is ionized. In the case of pyridine, a still stronger base, ionization occurs.

$$C_5H_5N + I_2 \rightleftarrows C_5H_5NI^+ \, I^-$$

$$C_5H_5N + HCl \rightleftarrows C_5H_5NH^+ \, Cl^-$$

Finally both "acids" unite with halide ions.

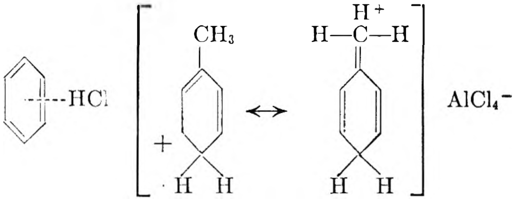
$$C_5H_5NH^+ \, I^- + I_2 \rightleftarrows C_5H_5NH^+ \, I_3^-$$

$$C_5H_5NH^+ \, Cl^- + HCl \rightleftarrows C_5H_5NH^+ \, HCl_2^-$$

The phenomena are so similar that I question the desirability of assigning the acceptor iodine ($x\sigma$) to an entirely different class ($h\sigma$) solely on the basis of a postulated difference in the nature of the bonding between hydrogen or iodine and the donor molecule. If it is desirable to organize these phenomena into distinct classes, I believe that the classification should be based primarily upon experimental similarities and differences, rather than upon hypothetical differences in the nature of bond involved. (Frankly, I doubt whether our understanding of and agreement in the field of chemical bonding has yet reached the point where we can safely use it as a basis for classification of donor-acceptor interaction.)

To illustrate this point let us consider the complexes formed by aromatic hydrocarbons with hydrogen chloride on the one hand and by hydrogen chloride–aluminum chloride on the other. In the case of the hydrogen chloride–aromatic complexes, we observe that they are both formed and dissociated rapidly at −80°, they are colorless, they do not exchange deuterium with the aromatic, and they do not conduct the electric current. On the other hand, the hydrogen chloride–aluminum chloride aromatic complexes form and dissociate slowly at −80°, are intensely colored, exchange deuterium rapidly, and are excellent conductors of the electric current.

We have applied the term π-complexes to the hydrogen chloride–aromatic species and other related complexes, and have proposed the term σ-complexes for derivatives of the HCl–$AlCl_3$ type.



π-complexes σ-complex

Apart from the preference one may have for his own terminology and classification, it appears to me far safer to base any classification upon similarities and differences in chemical behavior which are directly observable in the laboratory, rather than upon assumed similarities and differences in chemical bonding.

Finally I should like to call attention to the dangers involved in adopting any elaborate system of notation such as that proposed by Professor Mulliken. Experts working in the field would have little difficulty in mastering and utilizing a large group of specialized symbols. There is little doubt that communication among the specialists would be somewhat facilitated by such a shorthand once it is mastered. However, there is also little doubt that this increased ease of communication among the specialists will be accompanied by a serious loss in communication with workers in other fields of chemistry who would doubtless find too burdensome the task of mastering and using so many specialized symbols. Since the phenomena associated with acids and bases (or donors and acceptors) are of the utmost importance to practically all fields of chemistry, it is clear that any new phenomena and ideas which are uncovered in this area should be readily communicable to all chemists who may wish to coördinate these findings with their own investigations. I question whether the relatively minor advantage of an increased ease of communication among specialists would be a reasonable price to pay for a serious decrease in the ease of communication with workers in related areas.

I

R. S. **MULLIKEN**.—Professor Brown's feeling that my classification of donors and acceptors may be excessively elaborate has caused me to revise the original mimeographed version of the manuscript prepared for the meeting. I have added two brief introductory tables (I and II in the printed version), which I think show that the basic classification (π, σ, n and R donors, and π, σ, v and Q acceptors) is relatively simple. The four elaborate and detailed tables of the original version have now been somewhat clarified and placed at the end as an Appendix.

However, perhaps Professor Brown also had in mind the fact that intermediate cases in the classification are frequent (see, for example, some of the Remarks in Table IV). He asked, in conversation, why it is necessary ever to classify such molecules as the alkyl halides as σ donors; why may one not simply suppose that RX always functions (through its X atom) as an n (onium) donor? Thus (here *cf.* Section 4 in Table VI) why not

$$RX + BX_3 \longrightarrow (RX \rightarrow BX_3) \longrightarrow R^+BX_4^-$$

presumably with an unstable intermediate analogous in structure to the stable product known from the work of Brown and his collaborators (*cf.* Table VI, Section 1 and footnote *e*) to be formed in such a reaction as

$$RBr + GaBr_3 \longrightarrow RBr \rightarrow GaBr_3?$$

Actually, both the suggested intermediate in the first and the final product in the second of these reactions must contain (among others) important resonance components of the *two types* $R—X^+—^-AX_3$ and $R^+X - {}^-AX_3$, of which the first corresponds to n functioning and the second to σ functioning of the donor.

Since it is not always easy to decide in such cases which (if either) resonance component strongly predominates, it is then often safest to make the classification by saying that the given donor or acceptor is functioning in a manner intermediate between those of two specified pure classes. I do not feel that even a somewhat frequent occurrence of intermediate cases destroys the value of a significant classification scheme, since much of this value lies in the insight one obtains just in the process of attempting a classification.

Referring again to the first of the two reactions mentioned above, it is clear that RX is functioning in the *over-all* reaction as a pure dissociative σ (*i.e.*, σ_d) donor, even though in an intermediate stage it may be acting partly like an n donor. One may, however, ask whether the reaction actually proceeds bimolecularly straight through in one sweep to the final ion-pair product, or in distinct stages of which the first might conceivably bo a bimolecular reaction to form an intermediate of the type indicated above. Or does it go quasi-unimolecularly in a familiar way involving as a first step the ionization of RX in solution to $R^+sl + X^-sl$? These alternatives illustrate the fact that the functioning of a given donor (or acceptor) in a particular reaction which proceeds in distinct stages may be classified either in terms of its behavior in the initial stage, or in terms of the over-all reaction. As is well known, reactions of a given over-all type may in general proceed by any of a variety of mechanisms, often with two or more competing mechanisms operative at substantial rates in one and the same reaction vessel. As is also well known, our present knowledge as to precisely what mechanisms are actually most important in individual reactions under specified conditions is still very limited.

In the list of examples of donor–acceptor reactions in Table VI of my paper, my intention was to base each classification if possible on what seemed the most likely *first distinct stage* in the reaction under fairly usual conditions; but I may not have been wholly consistent in this. (My intention and point of view are explained in detail in the last paragraph of the notes to Table VI.) In any event, I believe that the proposed classification scheme, if it proves worth while at all, may be useful in the analysis and classification *both* of reaction mechanisms and of over-all reactions.

II

With Professor Brown's comment that the acceptor types of which I_2 and HCl are representatives show closely parallel empirical behavior in the formation of loose complexes, I cannot seriously disagree. In fact, I originally (see ref. 2 in my paper) had classed these types together as *d* acceptors, but later (*cf.* footnote 53 of ref. 2, and ref. 3) after a good deal of thought concluded that they should be rated as distinct subclasses ($x\sigma$ and $h\sigma$) of the σ acceptor class. This conclusion was based on the three following considerations.

(A) Much weaker acceptor properties are to be *expected theoretically* for the $h\sigma$ than for the $x\sigma$ group, in view of the much larger bond strengths and smaller electron affinities for the former; the relevance of these factors can be seen by reference to Fig. 1 and eq. (5) of ref. 3 taken in connection with the general theory of donor-acceptor interaction energies in ref. 2. (B) The loose HCl complexes do not appear to differ empirically in any essential way from numerous other loose complexes which are generally agreed to be hydrogen-bonded complexes of essentially electrostatic character: see Section 19 and related footnotes in Table VI. (C) The $x\sigma$ subclass is set apart by the fact that its loose complexes with both n and π donors show characteristic ultraviolet spectra of their own, of which the λ 2900 absorption found by Benesi and Hildebrand is the classical example; and the best explanation (*cf.* ref. 2) appears to be that these are charge transfer spectra of definitely donor–acceptor complexes. No corresponding spectra of hydrogen halide complexes have been reported, and it is my prediction, derived from the theoretical considerations mentioned under (A), that no such spectra are likely to be found.

However, Professor Brown's comment has caused me to revise somewhat, for the printed version, the discussion as given in the original mimeographed copy, by making use of the terminology "outer complexes" for loose addition compounds of both the $x\sigma$ and $h\sigma$ types, regardless of whether charge transfer or other forces may be principally responsible for the formation of these complexes. This considerably simplifies the presentation and enlarges the applicability of Fig. 2. At the same time, I continue to maintain (subject always to correction if new evidence requires) that the $x\sigma$ and $h\sigma$ acceptors are very different in respect to the major forces which make them associate with donors, as well as in certain empirical, particularly spectroscopic, properties.* On the other hand, I believe that the fact that the $x\sigma$ and $h\sigma$ acceptors are in many respects similar in their complexing properties is appropriately recognized in classifying them both as subclasses of a single major class, the σ acceptors.

III

Professor Brown has proposed to use the term "π-complexes" for what I would call $b\pi$, $h\sigma$ *outer complexes*, and the term "σ-complexes" for what I would call v-assisted $b\pi$, $h\sigma$ *inner complexes* (with, in particular, HCl representing $h\sigma$). While I completely agree with Professor Brown's opinions† that his "π-complexes" are loose complexes and that his "σ-complexes" are intermediates of carbonium-salt type, with these two states of interaction separated by an activation barrier, I feel that his terminology is open to several objections. I would rather first classify the donor and acceptor each according to its initial structure, and then use terminology such as "outer complex" or "inner complex," as proposed in ref. 3 and further developed in the present paper, to distinguish between the two characteristic ("associative" and "dissociative") modes of interaction which I think occur for many types of donor, acceptor pairs.

---

* Another reason for setting apart the subclass $h\sigma$ is that it is identical with the important class of neutral molecule H-acids. Except for the distinctive chemical interest of the H-acids, the empirically and theoretically similar subclasses $h\sigma$ and $k\sigma$ (alkyl halides, *etc.*,) might well be lumped together.

† As expressed in more detail by Brown and Brady *J. Am. Chem. Soc.*, **74**, 3570 (1952). I am indebted to Professor Brown for letting me see a copy of this paper at the time of the Notre Dame meeting. In the present and in a previous paper (ref. 2), I have drawn heavily for examples, evidence, and suggested explanations on the very instructive and important work reported in numerous papers by Professor Brown and his students.

THE EFFECTS OF ISOTOPIC SUBSTITUTION ON THE RATES OF CHEMICAL REACTIONS[1]

BY JACOB BIGELEISEN

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York

Received May 17, 1952

A review is presented of the general theory of the effect of isotopic substitution on the rates of chemical reactions. The theory is based on the application of quantum statistics to the transition state method of Eyring, Polanyi and Wigner. The theory is applied to intramolecular isotopic reactions $A'B + AR \leftarrow R + ABA' \rightarrow AB + A'R$, where A and A′ are isotopes of the same element. Calculations for reactions of this type can be made without any models of the transition state and the only parameters necessary are the masses of A, B and A′. Good agreement is obtained with experiments in which combinations of C^{12}, C^{13}, N^{14}, N^{15}, O^{16} and O^{18} compose the bonds which are ruptured. In view of the agreement between theory and experiment, and the fact that no empirical parameters are introduced into the former, we may consider these experiments the best test of the transition state method in reaction kinetics made thus far. New calculations are presented for the effect of C^{13} substitution on the rate of decarboxylation reactions. The model chosen is the one used previously.[16] Good agreement is obtained with experiment. Similar calculations on the effect of C^{14} substitution in the carbonyl group in a series of base-catalyzed reactions of the carbonyl group show good agreement with experiment. A discussion is given of the differences between C^{14} and C^{13} substitution for C^{12}. No theoretical explanation can be found for some experiments where the effect for C^{14} is considerably greater than twice that for C^{13}.

Introduction

During the past four years there have appeared some twenty odd research papers dealing with the fractionation of the isotopes of the light elements, other than hydrogen, by virtue of differences in reaction rates. These differences in reaction rates are small and are of the order of 1–10%. By the use of differential methods with modern isotope ratio mass spectrometers or ion chambers this small effect can be measured to a few per cent. of the effect, corresponding to a precision of the order of 0.1% in the ratio of rate constants.

The experimental data which I wish to discuss have all been published, and I shall, therefore, omit any discussion of the actual experimental techniques and measurements, even though they constitute a considerable research effort and accomplishment. What I wish to discuss is our understanding of these differences in reaction rates and what some of the successes and limitations of the theory are at present.

Application of the Transition State Method to the Relative Rates of Reaction of Isotopic Molecules

The transition state method in chemical kinetics dates back to the important paper by Marcelin.[2] This method, which is widely accepted today, presupposes that there are a small number of activated molecules in equilibrium with the reacting species and that the rate of the reaction is controlled by the rate of decomposition of the activated species. The limitations of these assumptions have been discussed in detail at a symposium held in 1937 by the Faraday Society in Manchester[3] and in recent years by Kramers,[4a] Eyring and Zwolinski,[4b] and Hulburt and Hirschfelder.[5] These latter studies as well as the searching one by Wigner[6] suffice to show that we may proceed with confidence to apply the methods of quantum statistics to the transition state hypothesis. In the calculation of the number of activated molecules decomposing per unit time we will be limited by an approximation valid to terms containing h^4. This will not be any limitation of any consequence in considering isotope effects in elements other than hydrogen.[7]

The ratio of the rate constants for the reaction of isotopic molecules can, in principle, be calculated explicitly from the formulas given by Eyring[8] after correction for the tunnel effect or from the equivalent ones of Evans and Polanyi.[9] This method is applicable to the isotopes of hydrogen, where large relative rates are found, but even in this case the most significant factors which contribute to the differences in rates which result from isotopic substitution may be obscured. In fact, in the calculations carried out by Farkas and Wigner[10] on the relative rates of reactions of protium and deuterium atoms with the isotopic hydrogen molecules, it is recognized that some terms in the ratio of rate constants cancel others because of the fact that the potential energy surface for a reaction is invariant with respect to isotopic substitution. For their purposes it was not necessary to reduce the expression for the ratio of rate constants to a form where one would calculate the deviation of this quantity from unity directly. If one is to avoid errors in computation and desires an insight into the significant factors when dealing with the isotopes of elements other than hydrogen, then such a procedure is helpful and almost necessary.

This development has been carried out[11] by the application of a method developed by Bigeleisen and Mayer[7] for the calculation of isotopic equilibria. The only assumptions made are those inherent in the transition state hypothesis. One finds for the ratio of the rate constants of reactions involving isotopic molecules

---

[1] Research carried out under the auspices of the Atomic Energy Commission.

[2] A. Marcelin, *Ann. phys.*, **3**, 158 (1915).

[3] "Reaction Kinetics; A General Discussion," Gurney and Jackson, London, 1937.

[4] (a) H. A. Kramers, *Physica*, **7**, 284 (1940); (b) H. Eyring and B. Zwolinski, *J. Am. Chem. Soc.*, **69**, 2702 (1947).

[5] H. M. Hulburt and J. O. Hirschfelder, *J. Chem. Phys.*, **17**, 964 (1949).

[6] E. Wigner, ref. 3, pp. 29–41.

[7] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[8] H. Eyring, *ibid.*, **3**, 107 (1935).

[9] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

[10] L. Farkas and E. Wigner, *ibid.*, **32**, 708 (1936).

[11] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

$$\frac{k_1}{k_2} = \frac{S_1S_2^{\neq}}{S_2S_1^{\neq}}\left(\frac{m_2^*}{m_1^*}\right)^{1/2}\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n'-6} G(u_i^{\neq})\Delta u_i^{\neq}\right] \quad (1)$$

where k is the rate constant, S is a symmetry number, m^* is an effective mass of the molecule in transition state along the coördinate which leads to the products of the reaction, $G(u)$ is the free energy function of Bigeleisen and Mayer,[7] $3n - 6$ is the number of vibrational modes in the molecule, and Δu_i is equal to $hc(\omega_1 - \omega_2)/kT$. Because of the definition of $G(u)$ the subscripts 1 and 2 refer to the light and heavy molecules, respectively. The superscript $\neq$ refers to a property of the transition state. The ratio $(m_2^*/m_1^*)^{1/2}$ can be replaced by the ratio ν_{L1}/ν_{L2}, where ν_L is the imaginary frequency in the transition state.

The factor involving the S's is a simple statistical one which arises from the fact that if there are two or more identical atoms of the isotope in question in the molecule there will be a corresponding increase in the probability of one of them reacting. The factor $(m_2^*/m_1^*)^{1/2}$ or ν_{L1}/ν_{L2} gives the ratio of the number of light and heavy "activated complexes" which decompose per unit time. The quantity in the square brackets on the right of equation (1) gives a quantitative description of the effect of the differences in zero point energies of the light and heavy molecules in the normal and transition states. Equation (1) cannot be applied to the isotopes of hydrogen since it is derived from a more general equation by an expansion which is valid for the isotopes of all elements except hydrogen. For the isotopes of hydrogen equation (5) of reference (11) should be used. The free energy function $G(u)$ is equal to $(1/2 - 1/u + 1/(e^u - 1))$, where $u = hc\omega/kT$. This is a well behaved function with values between 0 and $1/2$ as u goes from zero to infinity. Convenient tables of the function are given in reference 7.

Intramolecular Isotope Effects

We consider a molecule to be represented by the formula ABA′, where the groups A and A′ are identical except for the isotopic constitution of one of its atoms. If this molecule undergoes some reaction with some substance, R, in which the A–B bond is broken, then the products will be AB and A′R or A′B and AR depending on whether the A′B or AB bond ruptures. The relative rates of these processes will be called an intramolecular isotope effect in accord with the terminology introduced by Lindsay, Bourns and Thode.[12] Several reactions of this type have been studied and we shall consider them first because of the simplicity of the theoretical treatment.

Usually a pure sample of ABA′ is not available for experimental investigation, nor is it necessary. If ABA′ is present as a dilute solution in ABA (of the order of 1%), then irrespective of the order of the reaction in ABA, the ratio of the rate constants k_4/k_3 for the processes

$$\mathrm{ABA'} + \mathrm{R} \xrightarrow{k_3} \mathrm{A'R} + \mathrm{AB}$$

$$\mathrm{ABA'} + \mathrm{R} \xrightarrow{k_4} \mathrm{AR} + \mathrm{A'B}$$

can be obtained from an intercomparison of the isotopic composition of AR or AB obtained from *complete* reaction and the substrate ABA.[13] An intercomparison of a sample of AR or AB obtained after a few per cent. reaction with the substrate will give the ratio of $k_1/2k_3$, where k_1 refers to the reaction

$$\mathrm{ABA} + \mathrm{R} \xrightarrow{k_1} \mathrm{AB} + \mathrm{AR}$$

For intramolecular isotope effects equation (1) becomes particularly simple. We may write formally

$$\frac{k_4}{k_3} = S\frac{\nu_{4L}}{\nu_{3L}}\left[1 + \sum_i^{3n-6} G(u_i)(u_{4i} - u_{3i}) - \sum_i^{3n'-6} G(u_i^{\neq})(u_{4i}^{\neq} - u_{3i}^{\neq})\right] \quad (2)$$

where S is the statistical factor. Since we are considering two alternate modes of reaction of the molecule ABA′, $u_{4i} = u_{3i}$, and, of the terms in the brackets in equation (2), we need only consider $\sum_i^{3n'-6} G(u_i^{\neq})(u_{4i}^{\neq} - u_{3i}^{\neq})$. For some simple reactions it is possible to construct potential energy surfaces for the reaction and in principle calculate this latter quantity. However, even for reactions involving a total of three atoms some approximations must be made, which might take the form of the Heitler–London method or the molecular orbital method.

The reactions which we will consider contain many more atoms and a reasonable approximation can be made without recourse to such methods. If one considers isotopes of the first row elements in the periodic table one finds that the free energy function, $\sum_i^{3n-6} G(u_i)\Delta u_i$, amounts to about 0.10 to 0.20 at room temperature, and less at higher ones, for isotopes of an element which differ by one mass unit.[14] When the change in mass occurred by isotopic substitution is a small fraction of the atomic weight of the element, then the free energy function increases almost but not quite linearly with the change in mass. These differences of the order of 0.10 to 0.20 per unit increase in the neutron number result from large changes in the chemical bonding of the element. In fact they refer to the difference between some chemical compound and the uncombined gaseous atom. We wish to evaluate the free energy function for a pair of isotopic isomers in the transition state. Where reliable estimates can be made for normal molecules from spectroscopic data, even for the isotopes of hydrogen one finds this difference is very small.[15] It is therefore reasonable and appropriate to neglect the term $\sum_i^{3n'-6} G(u_i^{\neq})\Delta u_i^{\neq}$ for intramolecular isotopic reactions.

The ratio of the rate constants, k_4/k_3, reduces to

$$k_4/k_3 = S\nu_{4L}/\nu_{3L} = S(m_3^*/m_4^*)^{1/2} \quad (3)$$

---

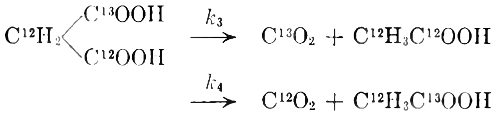
[12] J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **29**, 192 (1951).

[13] J. Bigeleisen, *Science*, **110**, 14 (1949).

[14] *Cf.* the tabulation by H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[15] See the discussion by J. Bigeleisen, *Can. J. Chem.*, **30**, 443 1952.

This ratio is independent of temperature and the first prediction we get from theory is that there should be no temperature coefficient to intramolecular isotopic reactions.[16] This prediction has been confirmed by the work of Lindsay, Bourns and Thode[12] on the C^{13}-isotope effect in the decarboxylation of malonic acid.



$$C^{12}H_2\begin{cases}C^{13}OOH\\C^{12}OOH\end{cases}\xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}OOH$$
$$\xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH$$

Their results are presented in Table I.

TABLE I

INFLUENCE OF TEMPERATURE ON THE INTRAMOLECULAR ISOTOPE EFFECT IN MALONIC ACID DECARBOXYLATION

T, °C.	138	151	174	199
k_4/k_3	1.020	1.020	1.024	1.021

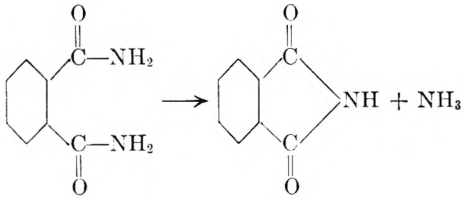
The value of $m^{*1/2}$ or the ratio ν_{4L}/ν_{3L} can be calculated from a theorem due to Slater.[17] Comparisons between theory and experiment are given in Table II.

Table II includes all of the data published in the literature except for some calculations by Pitzer[18] on reactions (2) and (3). These calculations are not applicable to intramolecular isotope effects[19] and are therefore omitted. No theoretical value for the dehydration of oxalic acid by sulfuric acid is included because the rate of the reaction in the neighborhood of 100% H_2SO_4 cannot be explained even by the theory of general acid catalysis.[27] Above 0.6% H_2O in H_2SO_4 the acid catalysis can be explained by the H_0 function of Hammett.[28]

Except for reactions (2) and (3), where there is considerable disagreement in the experimental data or where it can be shown that the experimental data must be in error,[29] it is obvious that the agreement between theory and experiment is within the limit of the experimental errors. We may note that the theoretical calculations employ no empirical parameters and utilize only the masses of the atoms in the bonds ruptured in the reaction. This agreement constitutes the most direct substantiation of the transition state method which has been afforded to date. Furthermore, the method of calculation was outlined prior to the experimental work except for reactions (2) and (3), where there is poor agreement.

TABLE II

INTRAMOLECULAR ISOTOPE EFFECTS

Reaction	Bonds intercompared	T, °C.	k_4/k_3 experimental	k_4/k_3 theoretical
	C^{12}–C^{12}		1.020 ± 0.001[20]	
1, $CH_2(COOH)_2 \longrightarrow CO_2 + CH_3COOH$	*vs.*	138	1.021 ± .001[12]	1.020[20]
	C^{12}–C^{13}		1.026 ± .001[21]	
	C^{12}–C^{12}	150	1.12 ± .03[22]	
2, $CH_2(COOH)_2 \longrightarrow CO_2 + CH_3COOH$	*vs.*	153	1.06 ± .02[23]	
	C^{12}–C^{14}	138	1.087 – 1.105[21]	1.038[16]
3, $BrCH(COOH)_2 \longrightarrow CO_2 + BrCH_2COOH$	C^{12}–C^{12} *vs.* C^{12}–C^{14}	115	1.41 ± .08[22]	1.038[16]
4, $(COOH)_2 \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$		100	1.033 [24]	
5, $NH_4NO_3 \longrightarrow N_2O + 2H_2O$	N^{14}–O^{16} *vs.* N^{14}–O^{18}	220	1.023 ± .003[25]	1.026[25]
6, 	C^{12}–N^{14} *vs.* C^{12}–N^{15}	136	1.015 ± .001[26]	1.016[15]

Intermolecular Isotope Effects

The reactions considered in the preceding section, intramolecular isotope effects, are rather special and we shall now turn to the more general case of intermolecular isotope effects. Examples of such reactions are

$$\left.\begin{array}{l}C^{12}H_2(C^{12}OOH)_2 \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OOH\\ C^{12}H_2(C^{12}OOH)(C^{13}OOH) \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}OOH\end{array}\right\}$$

---

[16] J. Bigeleisen, *J. Chem. Phys.*, **17**, 425 (1949).

[17] N. B. Slater, *Proc. Roy. Soc.* (*London*), **194**, 113 (1948).

[18] K. S. Pitzer, *J. Chem. Phys.*, **17**, 1341 (1949).

[19] A. A. Bothner-By and J. Bigeleisen, *ibid.*, **19**, 755 (1951).

[20] J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

[21] P. E. Yankwich, E. C. Stivers and R. F. Nystrom, *ibid.*, **20**, 344 (1952).

[22] P. E. Yankwich and M. Calvin, *ibid.*, **17**, 109 (1949).

[23] A. Roe and M. Hellman, *ibid.*, **19**, 660 (1951).

[24] J. G. Lindsay, D. E. McElcheran and H. G. Thode, *ibid.*, **17**, 589 (1949).

[25] L. Friedman and J. Bigeleisen, *ibid.*, **18**, 1325 (1950).

[26] F. W. Stacey, J. G. Lindsay and A. N. Bourns, *Can. J. Chem.*, **30**, 135 (1952).

[27] J. Bigeleisen, paper presented at the Meeting of the American Chemical Society, Chicago, September, 1950.

[28] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 284.

[29] J. Bigeleisen, Brookhaven National Laboratory Conference on "Isotopic Exchange Reactions and Chemical Kinetics," December 1-3, 1948, BNL-C-8, p. 70.

$$\left.\begin{array}{l} Cl_3C^{12}C^{12}OO^- \xrightarrow{k_1} C^{12}Cl_3^- + C^{12}O_2 \\ Cl_3C^{12}C^{13}OO^- \xrightarrow{k_3} C^{12}Cl_3^- + C^{13}O_2 \end{array}\right\}$$

The theoretical treatment of reactions of this type is more difficult than the case of intramolecular isotope effects, since it will now be necessary to evaluate the free energy functions, $G(u_i)\Delta u_i$, for the normal molecules and the transition states. For this calculation one requires detailed knowledge of the vibrational frequencies of the molecule as affected by isotopic substitution. This information is not available even for the normal molecules of the substances which have been investigated experimentally. Therefore, the best that can be done at present, from a theoretical point of view, is to make some approximate calculations based on some model. The calculations will be limited by the model chosen.

Several years ago the writer proposed a model[30] to treat intermolecular isotope effects and applied it to the decarboxylation of malonic acid.[16,20] This model presumes that the only essential difference between the free energy functions of the normal and transition states, $\sum_i G(u_i)\Delta u_i$ and $\sum_i G(u_i^{\neq})\Delta u_i^{\neq}$, respectively, arises from the vibration frequency of the bond ruptured in the transition state. The force constant of this bond is set equal to zero in the transition state and all other frequencies are assumed to remain the same. This is a very rough approximation, indeed. The calculations published for this model gave 1.021 for the ratio of k_1/Sk_3 for C^{13} substitution for C^{12} in decarboxylation reactions, while the experimental values were found to be of the order of 1.035 for several different acids.[19] These calculations were rather rough and were not carried out in a consistent manner. Subsequently, Pitzer[18] refined the calculation and obtained a reasonable approximation to the free energy function for isotopic carbon substitution in carboxylic acids. His approximations for the transition state lead to a value of 1.07 for C^{13} substitution for the ratio k_1/Sk_3, which is also in poor agreement with experiment. In addition Pitzer's theoretical temperature coefficient is too large.

It has been shown in a study of the oxygen isotope effect on the rate of decomposition of NH_4NO_3[25] and in the thermal deammonation of phthalamide[15] that, while the bond being ruptured in the chemical reaction is weakened in the transition state, there are other bonds which are appreciably strengthened. If this phenomenon is a general one, it would practically invalidate the model discussed above. In any case it is clear that this model is not applicable to these reactions. The model has only one virtue, namely, that calculations can be readily made. In view of this, I would like to compare some such calculations with the experimental data.

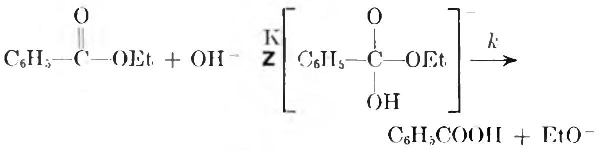
Decarboxylation Reactions.—The effect of C^{13} and C^{14} substitution in the carboxyl group on the rate of decarboxylation reactions has received considerable attention as a result of disagreement between different workers on some experimental as well as theoretical aspects of the problem. As a result, there is a moderate amount of data on acids of different structures, which decarboxylate either in acid or basic solution. The experimental results are summarized in Table III.

There can be little doubt about the accuracy of the C^{12} *vs.* C^{13} experimental data in Table III. The self consistency of the data from the individual laboratories is excellent and systematic errors are eliminated by the experimental method. Furthermore, intercomparison of the data from three independent laboratories shows agreement within the limits of the experimental error stated by each of them.

In the fifth column of Table III there are included some theoretical calculations of questionable reliability based on the model discussed above. These calculations differ from those published previously[16,20] in the estimated frequency shift incurred by isotopic substitution for the bond ruptured by the reaction. In the original calculations this was estimated by the treatment of the carboxyl group as a unit of mass 45 for C^{12} and mass 46 for C^{13}. To be self consistent with the rest of the calculations $\omega C^{12}/\omega C^{13}$ should be calculated from Slater's theorem. When this is done and a value of 900 cm.$^{-1}$ is used for the C–C stretching frequency,[16,31] one obtains the theoretical values in the fifth column of Table III. The agreement with experiment, except for the case of C^{14} substitution in mesitoic acid which will be discussed later, is surprisingly good and better than one should really expect in view of the approximations made.

Base-catalyzed Reactions of the Carbonyl Group.—There are a considerable number of base-catalyzed reactions of the carbonyl group. The mechanisms of many of these reactions are well established from structural, kinetic and tracer studies.[32] Stevens and Attree[33,34] have investigated a number of them for isotopic effects by C^{14} substitution in the carbonyl group. Their results will be considered in the light of the accepted mechanisms.

For the relative rates of hydrolysis of $C^{12}{=}O$ and $C^{14}{=}O$ ethyl benzoates a value of 1.16 ± 0.02 is found at room temperature.[36] The mechanism of the reaction is



$$C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OEt + OH^- \overset{K}{\rightleftharpoons} \left[C_6H_5{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{|}}{C}}{-}OEt\right]^- \xrightarrow{k} C_6H_5COOH + EtO^-$$

The ratio of the observed rate constants $k_{12\text{ obsd}}/k_{14\text{ obsd}}$ is therefore equal to

$$k_{12\text{ obsd}}/k_{14\text{ obsd}} = K_{12}k_{12}/K_{14}k_{14}$$

where K refers to the rapid equilibrium between the ester and hydroxide ion and k refers to the specific rate of decomposition of the addition product. The subscripts 12 and 14 refer to C^{12} and C^{14} in the carbonyl group, respectively. For reactions of the

---

(30) J. Bigeleisen, *J. Chem. Phys.*, **17**, 345 (1949).

(31) K. W. F. Kohlrausch, "Ramanspektren," Akademische Verlagsgesellshaft, Leipzig, 1943, p. 204.

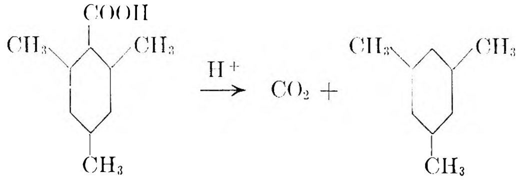
(32) See ref. 28, chapters 10 and 11.

(33) R. W. Attree and W. H. Stevens, *Can. J. Research*, **B27**, 807 (1949).

(34) W. H. Stevens and R. W. Attree, *J. Chem. Phys.*, **18**, 574 (1950).

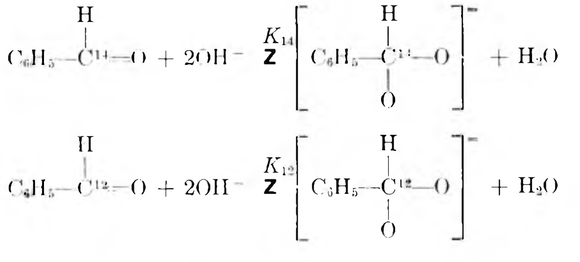
TABLE III

CARBOXYL-C^{13} AND -C^{14} INTERMOLECULAR ISOTOPE EFFECTS IN DECARBOXYLATION REACTIONS

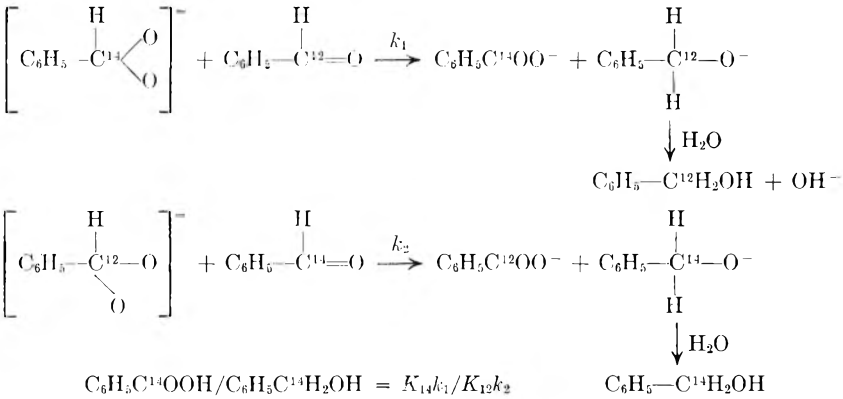
Reaction	Isotopes intercompared	T, °C.	k_1/Sk_3 experimental	k_1/Sk_3 theoretical
1, $CH_2(COOH)_2 \longrightarrow CO_2 + CH_3COOH$	C^{12} *vs.* C^{13}	138	1.037 ± 0.002 [20]	
	C^{12} *vs.* C^{13}	137	1.034 [35]	1.035
	C^{12} *vs.* C^{13}	149	1.041 [35]	
	C^{12} *vs.* C^{13}	173	1.034 [35]	
	C^{12} *vs.* C^{13}	196	1.036 [35]	1.031
2, 	C^{12} *vs.* C^{13}	61.2	1.037 ± .003 [19]	
	C^{12} *vs.* C^{13}	60	1.038 ± .001 [36]	1.041
	C^{12} *vs.* C^{13}	92.0	1.032 ± .001 [19]	1.038
	C^{12} *vs.* C^{14}	60	1.101 ± .007 [36]	1.078
3, $Cl_3C\text{–}CO_2^- \xrightarrow{OH^-} CHCl_3 + HCO_3^-$	C^{12} *vs.* C^{13}	70.4	1.0338 ± .0007 [37]	1.040

acid–base type it can be shown that the equilibrium constants for isotopic exchange are very close to classical statistics and that the heavy isotope usually concentrates in the species with the largest number of bonds attached to the element under consideration.[7] One would expect K_{12}/K_{14} to be of the order of (1/1.03–1/1.05) at room temperature. The ratio of k_{12}/k_{14} can be estimated by the method just discussed for intermolecular isotope effects in decarboxylation reactions and is 1.19. For this calculation we have utilized the fact that the C–O vibration in esters and ethers (this is the bond broken[38]) is of the order of 1700 cm.$^{-1}$. This leads to a theoretical value of $k_{12\ \text{obsd}}/k_{14\ \text{obsd}}$ of the order of 1.14 to 1.16, which is in good agreement with experiment.

In their study of the Cannizarro reaction on C_6H_5-$C^{14}HO$, Stevens and Attree find the C^{14} equally distributed (within ± 1.5%) between the benzoic acid and the benzyl alcohol. The relative yields of $C_6H_5C^{14}OOH$ and $C_6H_5C^{14}H_2OH$ can be expressed in terms of rate and equilibrium constants based on the mechanism of the reaction.

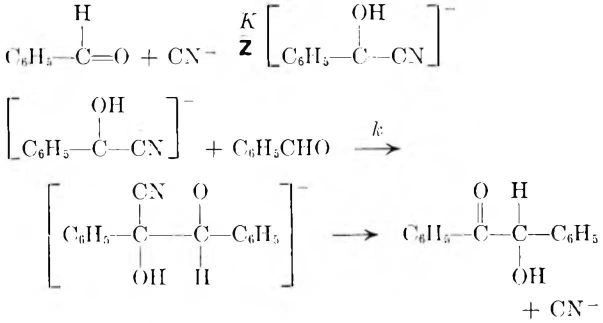


Since the rate-determining step involves a hydride shift[39] for which a negligible isotope effect has been predicted and found,[40] we can set k_1 equal to k_2 and theoretically we expect $C_6H_5C^{14}OOH/C_6H_5C^{14}H_2OH$ to be equal to K_{14}/K_{12}, which we have seen is of the order of 1.03 and in good agreement with the experimental results of Stevens and Attree.



$$C_6H_5C^{14}OOH/C_6H_5C^{14}H_2OH = K_{14}k_1/K_{12}k_2$$

In the benzoin condensation, about which there is no doubt in the mechanism



Stevens and Attree find the C^{14} equally distributed between the ketonic and alcoholic carbon atoms. It follows from this mechanism and the theory of the relative reaction rates of isotopic molecules that the ratio of the yields of C^{14}-ketone and C^{14}-alcohol, K/A, is equal to

---

(35) J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **30**, 163 (1952).

(36) W. H. Stevens, J. M. Pepper and M. Lounsbury, *J. Chem. Phys.*, **20**, 192 (1952).

(37) J. Bigeleisen and T. L. Allen, *ibid.*, **19**, 760 (1951).

(38) M. Polanyi and A. L. Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934).

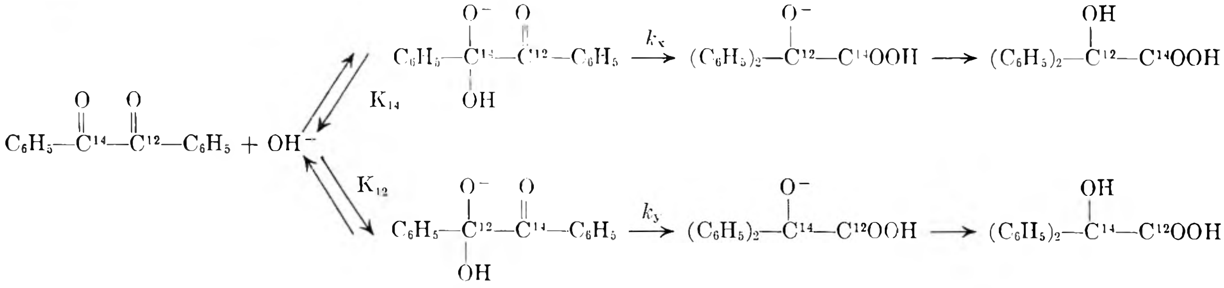
(39) H. Frederhagen and K. F. Bonhoeffer, *Z. physik Chem.*, **A181**, 379 (1938).

(40) A. A. Bothner-By, L. Friedman and J. Bigeleisen, Brookhaven National Laboratory Conference on "The Use of Tracers in Organic Reaction Mechanism Studies," January, 1950, BNL 44 (C-10), p. 39.

$$K/A = \left(\frac{m^*_{12\mathrm{CN}}}{m^*_{14\mathrm{CN}}}\right)^{1/2}\left(1 + \sum_i^{3n-6} G(u_i^{\neq})(u_i^{\neq}{}_{\underset{\mathrm{CN}}{C^{14}}-\underset{\mathrm{O}}{\overset{}{C^{12}}}} - u_i^{\neq}{}_{\underset{\mathrm{CN}}{C^{12}}-\underset{\mathrm{O}}{C^{14}}})\right)$$

Since the bond formed in the rate-determining step of the reaction is a C^{12}–C^{14} bond irrespective of whether the C^{14} finally appears as a ketone or alcohol, the reduced mass factor will be precisely unity. The free energy function reduces to the difference between isotopic isomers, which we have assumed in the preceding section on intramolecular isotope effects is negligible. In fact, this reaction might properly be discussed under that category. We, thus, arrive at the conclusion that there should be identical yields of the C^{14}-ketone and the C^{14}-alcohol in the benzoin condensation, in agreement with results of Stevens and Attree.

The benzilic acid rearrangement from benzoin, in which Stevens and Attree[37] find an 11% preference of the C^{14} for the α-carbon atom, is difficult to treat theoretically because of the complex changes which occur in the transition state of the slow step of the reaction. The reaction follows the mechanism



The ratio of the yields of $(C_6H_5)_2\overset{\displaystyle OH}{\overset{|}{C}}{}^{12}\text{—}C^{14}OOH$ and $(C_6H_5)_2\text{—}\overset{\displaystyle OH}{\overset{|}{C}}{}^{14}\text{—}C^{12}OOH$ is equal to $(K_{14}k_x)/(K_{12}k_y)$ in the above notation. It may be noted that the ratio K_{14}/K_{12} favors the production of C^{14} in the carboxyl group by about 3–5%. In the ratio of k_x/k_y there is no contribution from the reduced mass effect because a C_6H_5–C^{14} bond is broken and then followed by the formation of a C_6H_5–C^{12} bond in the reaction represented by k_x, while the inverse happens in the reaction followed by k_y. It has been shown by a rigorous thermodynamic argument that the isotope effect on the reduced mass factor is independent of whether the bond is formed or ruptured in the transition state.[15] When one considers the number of bonds rearranging in the course of this reaction, one would expect significant contributions from the free energy functions, and it is therefore not surprising that Stevens and Attree find an 11% effect in what at the outset might have looked like a simple intramolecular fractionation.

Relative Rates of C^{12}, C^{13} and C^{14}.—In the preceding section on C^{13}-isotope effects on decarboxylation reactions we have called attention to the fact that theory predicts that the effect in the comparison between C^{12} and C^{14} should be a little less than twice that of C^{12} and C^{13}. The experiments of Stevens, Pepper and Lounsbury[32] give a value of 2.7 ± 0.3 for the quantity $(k_{C^{12}}/k_{C^{14}}) - 1/(k_{C^{12}}/k_{C^{13}}) - 1$. The experiments of Yankwich, Stivers and Nystrom[21] show a similar, but larger, result for this ratio. It is therefore appropriate to inquire into this effect theoretically to search for an explanation.

One raises the question as to whether there might be some differences between the C^{14} and C^{13} systems as a result of the nuclear instability of the former. The effects of radiation from nuclear disintegration will tend to decrease the ratio $(k_{12}/k_{14}) - 1/(k_{12}/k_{13}) - 1$ rather than increase it, since the cross sections of C^{12}, C^{13} and C^{14} are identical for electrons and X-rays. Any effects from nuclear recoil and hot atom effects are negligible in experiments carried out in less than one year with a nucleus of 5700 year half-life. There are, therefore, no apparent effects from nuclear instability.

It is well known that differences in nuclear spins can produce no differences in the chemical properties of the isotopes of all the elements except for hydrogen or in the region below 10°K.[7]

In chemical kinetics one deals with terms of the form in which some numbers are raised to a power or appear in the exponential. The mass of some atom involved in the reaction will enter in these forms in some complicated way. In the deviation at the ratio of rate constants from unity, $(k_M/k_{M+\Delta M}) - 1$, a Taylor expansion can be carried out in $\Delta M/M$ and one will obtain as the leading term something proportional to $\Delta M/M$. Higher terms are negligible. Thus for isotopes of the same element, the effect on the reaction rate should be proportional to ΔM to a good approximation. This is not in agreement with the experiments of Stevens, Pepper and Lounsbury[32] nor those of Yankwich, Stivers, and Nystrom.[21] In the latter case some doubt is cast by the results of Roe and Hellman.[23] If this effect is a real one, it poses a very interesting problem.

CHARGE TRANSFER AND THE MOBILITY OF RARE GAS IONS

By J. A. HORNBECK

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

Received March 15, 1952

Ion–atom collisions in the rare gases between an atomic ion and a parent gas atom, such as Ne^+ and Ne, involve quantum mechanical symmetry effects which though rigorously inseparable have been listed as (a) a force of resonance attraction, (b) a force of resonance repulsion, and (c) charge exchange. Drift velocity measurements at high fields show that this complicated interaction may be represented to a good approximation by the hard sphere model of kinetic theory in which the collision cross section is several times the viscosity cross section of the atoms themselves.

In 1905 Langevin[1] published the first accurate mathematical theory of the mobility of positive ions in a gas. He showed that the ion drift velocity depends on the processes by which momentum is transferred at a collision between an ion and a gas molecule. Charge exchange, which probably was not envisaged in his day, is such a process of momentum transfer. It would not be surprising, therefore, if the combination of mobility theory and experiment should yield direct information about a charge transfer process. This in fact turns out to be the case. The reason for this, as we shall illustrate in this paper, is that charge transfer and associated effects can be so large that they dominate other energy loss mechanisms, as in the important case of the mobility of atomic rare gas ions moving in the parent gases.

Historical Background.—Mass spectrometer measurements gave the first experimental evidence of charge transfer in a gas. Harnwell,[2] for example, found processes of the type

$$A + Ne^+ \longrightarrow A^+ + Ne + KE$$

Kallmann and Rosen[3] apparently were the first to study charge transfer between a gas molecule and an ion with an identical core as, for example, between the atomic argon ion A^+ and an argon atom or between N_2^+ and N_2 (but not N^+ and N_2). On account of the high degree of particle symmetry in this case resonance effects occur which make it especially important, and it often has been called the Kallmann–Rosen effect. In the remainder of this paper we shall be concerned only with this resonance type of charge exchange and its connection with ionic mobility.

Mitchell and Ridler[4] working in Tyndall's laboratory at Bristol published what is apparently the first experimental proof that resonance charge transfer reduces the mobility of an ion in its parent gas. They studied the mobility, defined as the radio of drift velocity to electric field, of many different ions in nitrogen gas. Figure 1 is a reproduction of their data on the mobility of ions in nitrogen as a function of ionic mass. All of their results fall on a smooth curve that agrees well for the most part with the Langevin theory except the data for an ion produced when a glow discharge of nitrogen itself was used as the ion source in the apparatus. They reasoned that the ion in question was prob-

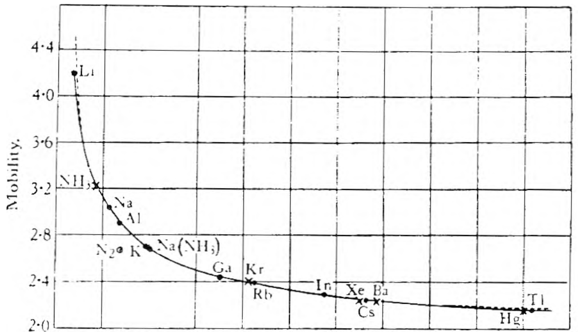


Fig. 1.—The mobility in cm.^{2}/volt-sec. at standard pressure and room temperature of ions in nitrogen as a function of ionic mass (Mitchell and Ridler).

---

[1] P. Langevin, *Ann. chim. phys.*, **8**, 238 (1905).

[2] G. P. Harnwell, *Phys. Rev.*, **29**, 683, 830 (1927).

[3] H. Kallmann and B. Rosen, *Z. Physik*, **61**, 61 (1930).

[4] J. H. Mitchell and K. E. W. Ridler, *Proc. Roy. Soc. (London)*, **A146**, 911 (1934).

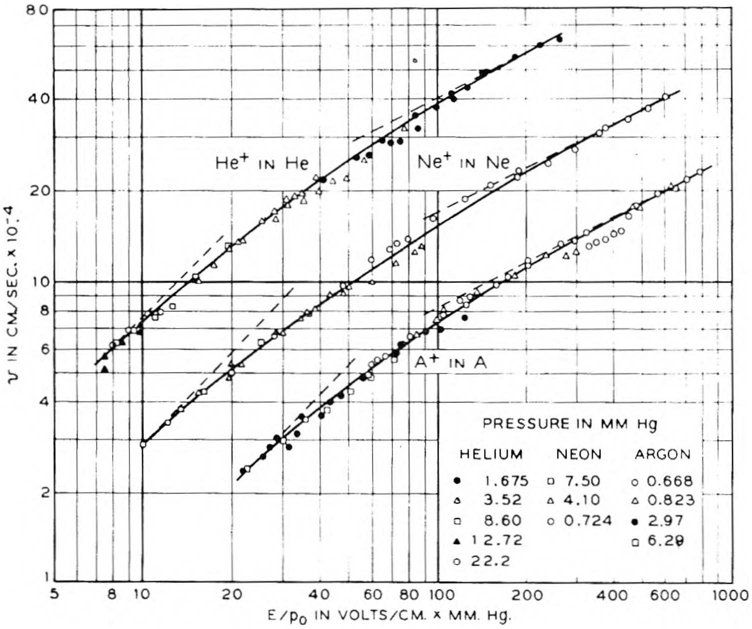


Fig. 2.—The drift velocity of atomic ions in helium, neon, and argon as a function of E/p_0. The broken lines at the left of each experimental curve have slope = 1, whereas the broken lines at the right have slope = 1/2.

ably N_2^+ and that its mobility was 7.5% low because of charge exchange.

In the rare gases charge transfer and its associated effects have special historical significance because they have contributed to the uncertainty regarding the correct values of the mobilities of atomic ions moving in the parent gases. In fact only recently have these values been established. Some years ago Massey and Mohr[5] obtained a value for the mobility of He^+ in He from a theory that included all the symmetry effects of this special case. Their result, however, was only slightly more than one-half the value obtained previously by Tyndall and Powell[6] in a careful series of experiments. For many years thereafter the only explanation advanced for this discrepancy was that the theory was in error because of an over-estimate of the effect of exchange forces (through the assumption that the mean period of electron exchange during the passage of the ion past an atom is small compared with the time of passage). The magnitude of the charge transfer effect as predicted theoretically undoubtedly seemed large in helium when compared to the nitrogen experiment.

About a decade later Meyerott,[7] a theoretical student of Margenau at Yale, suggested that the explanation of this discrepancy might be that Tyndall and Powell studied the heavier molecular ion He_2^+, not He^+ as they surmised. Meyerott thought the theory was essentially satisfactory and that the ion found with a higher mobility must therefore be He_2^+, which should not experience the symmetry effects associated with He^+. Biondi and Brown[8] added confirmation to this viewpoint by obtaining with a newly developed high frequency technique a mobility value for an ion in helium which, although somewhat larger than the Massey–Mohr value, differed greatly from that of Tyndall and Powell. Shortly thereafter measurements[9] in these laboratories showed the simultaneous presence of both atomic and molecular rare gas ions of helium, neon and argon and confirmed by mobility measurements the theory of Massey and Mohr and also the Bristol measurement on He_2^+. Thus we have today a consistent picture of the mobilities of rare gas ions based on the identification of both atomic and molecular ions in these gases and on the role of charge transfer effects.

Interaction Forces.—The drift velocity of an ion in a gas depends on three things: (a) the interaction forces between the ion and gas molecule at a collision, (b) the gas temperature, and (c) the magnitude of electric field E, or more accurately E/p_0, where p_0 is the gas pressure reduced to 0° and therefore is a measure of the gas number density. In an ordinary case such as K^+ in argon or A_2^+ in argon the major interaction forces are gas kinetic repulsion and polarization attraction. The first of these two forces can be represented in many cases by a model in which the ion and atom (or molecule) are hard elastic spheres whose closest distance of approach is fixed by the sum of the radii of the colliding particles. Polarization attraction arises because an ion induces a dipole moment on a neighboring atom and thereby attracts it.

Both of these forces exist between A^+ and an argon atom, but in this case there are in addition forces associated with the identity of the cores of the two particles. Massey and Mohr[5] pointed out in the analogous case of He^+ in He that the symmetry effects include a force of resonance attraction, an identical force of the opposite sign, *i.e.*, resonance repulsion, and charge exchange which is the shuttling of an electron back and forth between an ion and atom during a collision. Rigorously these effects cannot be separated in the theory, so it is improper to attribute the decrease in the mobility of the atomic ion to charge transfer alone. Perhaps a more accurate statement is that the additional symmetry effects increase the cross section of the atomic ion–atom collisions and thus decrease the drift velocity of these ions. The effect has been found[10] in all the rare gases.

Dr. Holstein in the following paper presents the mobility theory for argon and neon, and we shall not dwell further on this aspect of the question. In the remainder of this paper we shall present quantitative data that suggest a model for the symmetry interaction which is applicable in the high field region. These data also illustrate the agreement between theory and experiment in helium, neon and argon.

Cross Section for Resonance Charge Transfer.—Drift velocity measurements[11] on atomic rare gas

---

(5) H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc. (London)*, **A144**, 188 (1934).

(6) A. M. Tyndall and C. F. Powell, *ibid.*, **A134**, 125 (1931).

(7) R. Meyerott, *Phys. Rev.*, **70**, 671 (1946).

(8) M. A. Biondi and S. C. Brown, *ibid.*, **75**, 1700 (1949).

(9) J. A. Hornbeck, *ibid.*, **80**, 297 (1950).

(10) R. N. Varney, private communication, has recently studied krypton and xenon.

(11) J. A. Hornbeck, *Phys. Rev.*, **84**, 615 (1951).

ions in the parent gases have been carried out as a function of the parameter E/p_0. These data show that in the limit of low E/p_0 the drift velocity v_d approaches proportionality to E/p_0 (constant mobility region), while at high E/p_0, v_d varies directly as $(E/p_0)^{1/2}$. Dimensional arguments permit one to conclude from this last result that λ, the mean free path for ion–atom collisions, has become approximately constant. If in addition the law of scattering is isotropic to a good approximation, as Wannier[12] believes to be the case, the hard sphere model of kinetic theory would apply to this "high field" region because isotropy and a constant λ uniquely characterize this model.

The problem of ionic motion in high fields has been solved by Wannier[13] for the hard sphere model. He finds for the drift velocity $v_d = 1.147\ (a\lambda)^{1/2}$. Here a is the acceleration of the ion due to the electric field and $\lambda = 1/N\sigma_i$ where N is the gas number density and σ_i the hard sphere cross section. This formula has been applied[12] to the data, Fig. 2, and yields the values of σ_i listed in Table I. The viscosity cross section σ_a of the gas atoms is given in the second column for comparison.

TABLE I

HARD SPHERE CROSS SECTION σ_i AND VISCOSITY CROSS SECTION σ_a

	$\sigma_i \times 10^{16}$, cm.^{2}	$\sigma_a \times 10^{16}$, cm.^{2}
Helium	54	15
Neon	65	21
Argon	134	42

The fact that in each case σ_i is several times larger than gas kinetic cross section, as represented by σ_a, leads us to associate σ_i primarily with the symmetry effects rather than gas kinetic repulsion. Also polarization attraction need not be considered here because it is negligible[14] in the high field region. Thus σ_1 might well be called the cross section for resonance charge transfer in a hard sphere model for symmetry effects. Holstein[15] has pointed out that σ_i should not be exactly constant, but rather decrease slowly with increasing E/p_0. The experimental data of Fig. 2 are not accurate enough to show up this effect.

Low Field Mobility.—Extrapolation of the low field measurements, Fig. 2, to zero field yields the values of the "zero field" mobility, μ_0, listed in the first column of Table II. The second column contains theoretical values of μ_0, whereas in the third column for comparison are given the measured values of μ_0 for the molecular ions of the rare gases (He_2^+, Ne_2^+ and A_2^+).

TABLE II

ZERO FIELD MOBILITIES OF RARE GAS IONS IN THE PARENT GASES

	Atomic ion (exptl.) μ_0 (cm.^{2}/volt-sec.)	Atomic ion (theory) μ_0 (cm.^{2}/volt-sec.)	Molecular ion (exptl.) μ_0 (cm.^{2}/volt-sec.)
Helium	10.8	11[a]	19[c,d]
Neon	4.4	4.1[b]	6[d]
Argon	1.63	1.64[b]	1.9[d]

[a] Massey and Mohr, ref. 5. [b] T. Holstein, private communication. [c] Tyndall and Powell, ref. 6. [d] Hornbeck, ref. 9.

These results show the close agreement between theory and experiment for the mobilities of the atomic ions in the rare gases when symmetry effects are included in the theory. They also illustrate the magnitude of the symmetry effects in reducing μ_0 of the atomic ions compared to μ_0 of the molecular ions; for in the absence of these anomalous interactions μ_0 of the atomic ion would be something like $(3/2)^{1/2}$ *greater* than μ_0 of the corresponding molecular ion.

DISCUSSION

NORMAN DAVIDSON (Cal. Tech.).—For electron transfer processes in polyatomic systems, such as the aqueous ions to be discussed in later papers of this symposium, the Franck–Condon requirement decreases the probability of electron transfer because of the different internuclear distances in the exchanging partners. Charge transfer processes as reported in Dr. Hornbeck's paper should accordingly be less probable for diatomic or polyatomic gases than for monatomic gases. This conclusion seems to be borne out by the small effect for N_2^+ in N_2, as compared to the large effects for the rare gases.

---

(12) J. A. Hornbeck and G. H. Wannier, *Phys. Rev.*, **82**, 458 (1951).

(13) G. H. Wannier, *ibid.*, **83**, 281 (1951).

(14) The cross section associated with polarization attraction varies inversely as the collision velocity and therefore decreases with increasing field. Even at low fields the drift velocity is dominated by symmetry effects.

(15) T. Holstein, private communication.

MOBILITIES OF POSITIVE IONS IN THEIR PARENT GASES

By T. HOLSTEIN

Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

Received March 15, 1952

In this paper a method* is described for computing the mobility of an ion in its parent gas. Formulas of kinetic theory give the mobility in terms of the cross-section for *momentum-transfer* in an ion-atom collision. It is found that this cross-section is, in most cases, determined predominantly by charge exchange, which takes place readily between an ion and a parent atom. The computations require knowledge of the "resonance" or charge-excharge component of the total ion-atom interaction; the latter is obtained by a new method whose sole prerequisite is a knowledge of the Hartree-Fock wave function of the outermost atomic shell. The theory has been applied to the cases of neon and argon.

In calculating the mobilities of positive ions in gases, one has essentially two problems to solve. The first of these is the computation of the cross-section for collision between ions and neutral atoms. Knowing this cross-section, one has then to carry out a kinetic theory analysis involving the energy distribution of the ions and gas atoms.

In the case of sufficiently low external electric fields, to which the present paper applies, the kinetic theory part of the problem has been solved. In particular, for the case of ions in their parent gas, the mobility K, defined as the drift velocity per unit electric field, is given by the expression[1]

$$K = (3\pi^{1/2}/8)e/(MkT)^{1/2}N\ [Q_{\mathrm{M}}]_{\mathrm{av.}} \qquad (1)$$

In this relation N is the gas density, T, the absolute temperature, M, the common mass of an ion or atom and $[Q_{\mathrm{M}}]_{\mathrm{av.}}$, the "average cross-section for momentum transfer" defined as

$$[Q_{\mathrm{M}}]_{\mathrm{av.}} \equiv (1/2)(kT)^{-3}\int_0^\infty E^2 Q_{\mathrm{M}}\, e^{-E/kT}\, \mathrm{d}E \qquad (2)$$

where E is the kinetic energy of relative motion of an ion with respect to an atom, and Q_{M} the "monochromatic" momentum-transfer cross-section in an ion-atom collision. Q_{M} is itself defined by the relation

$$Q_{\mathrm{M}} = \int_0^\pi q(\theta)(1 - \cos\theta)\mathrm{d}\theta \qquad (3)$$

where $q(\theta)\ \mathrm{d}\theta$ is the differential cross-section for scattering between angles θ and $\theta + \mathrm{d}\theta$ in the center-of-gravity system of the colliding ion and atom.

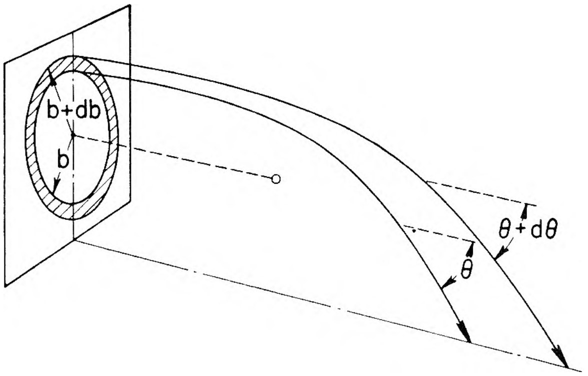


Fig. 1.—Classical theory of atom-ion scattering: the trajectories depicted here are those of the ion relative to the atom (open circle).

Q_{M} differs from the conventional Ramsauer collision cross-section in that the latter does not contain the factor $(1 - \cos\theta)$ which is a measure of the fraction of momentum lost by an ion in colliding with an atom. The difference between the two cross-sections will be particularly pronounced when the scattering, as given by $q(\theta)$, is predominantly in the forward direction.

It will be helpful in our further discussion to consider the mass motion of the atoms and ions as classical. This approximation not only considerably simplifies the treatment but is actually quite good except, perhaps, for the lightest atoms. The reason is that nuclear de Broglie wave lengths are generally small compared to the dimensions over which the ion-atom interaction suffers appreciable variation.

The classical formulation of the scattering process is illustrated in Fig. 1. Here are shown, in schematic fashion, two possible trajectories of the ion with respect to the atom. According to classical mechanics the scattering angle, θ, is a unique function of the "impact-parameter," b, *i.e.*, the initial moment arm of the ionic orbit with respect to the atom. b is conveniently represented, as shown in Fig. 1, in a "target plane" perpendicular to the initial relative velocity. It is then clear that the chance that a particle be scattered through an angle between θ and $\theta + \mathrm{d}\theta$ is equal to the chance that it impinge on the shaded strip indicated in Fig. 1. The area of this strip, *i.e.*, $2\pi\ b\mathrm{d}b$ may for our purposes be considered as the definition of the differential cross-section[2] $q(\theta)\ \mathrm{d}\theta$. We are thus able to formulate the momentum-transfer cross-section in the alternate form

$$Q_{\mathrm{M}} = \int_0^\infty (1 - \cos\theta)2\pi b\ \mathrm{d}b \qquad (4)$$

which will be more useful for our purposes.

It would now appear that one has merely to determine θ as a function of b in order to compute (4). However, in the case at hand, namely, the scattering of ions by atoms of the parent gas, the additional process of *charge-exchange* has to be taken into account; it turns out that this process affects the momentum transfer between a colliding ion-atom pair in a decisive way.

The ease of occurrence of charge-exchange between an ion and a parent atom arises from the circumstance that, in the absence of interaction, the electronic energy of the system does not depend

---

* Preliminary notice T. Holstein, *Phys. Rev.*, **82**, 567 (1951).

(1) Equations (1) and (2) of our paper are transcriptions of equations (6), (7) and (9) of the article by H. S. W. Massey, *Reports on Progress in Physics*, **12**, 248 (1949). An equivalent formulation is given in Chapter XII of "The Theory of Atomic Collisions," N. F. Mott and H. S. W. Massey, Second Edition, Oxford, 1949.

(2) As pointed out in the two references of footnote 1, $q(\theta)\mathrm{d}\theta$ is defined formally as the number of particles scattered between θ and $\theta + \mathrm{d}\theta$ per second per unit incident current density by a single scatterer.

upon the location of the charge. In other words, the state in which atom A is neutral and atom B ionized is energetically equivalent to the state in which A is ionized and B is neutral. As a result, the weakest electron-transfer interaction between A and B, if given sufficient time, will cause charge-exchange.

The effect of charge exchange upon the momentum-transfer cross-section is illustrated in Fig. 2. The scattering event therein depicted is one in which A, initially an ion, is scattered by B, which is initially neutral; the scattering angle in the center-of-gravity system is θ. It is then clear that, if, in the course of collision, charge exchange takes place, making A neutral and B the ion, the *effective* scattering angle will be $\pi - \theta$. If, in particular, the probability of charge exchange is $^1/_2$, the angular distribution of scattered ions is symmetrical about $\theta = 90°$, *regardless* of the angular scattering pattern of the atoms; the factor $(1 - \cos\theta)$ may then be equated to unity.

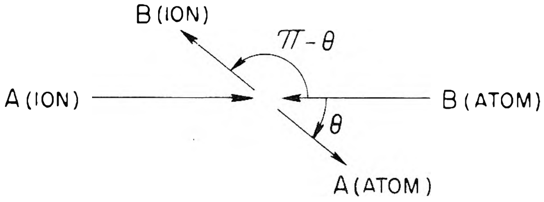


Fig. 2.—Effect of charge exchange on scattering angle.

The significance of these latest remarks becomes immediately apparent when we examine the nature of the charge-exchange process. As will later be shown, there exists a critical impact-parameter, b_c, which is the maximum b for which the probability of charge-exchange, P_{ex}, is equal to $^1/_2$. For $b < b_c$, P_{ex} is a rapidly oscillating function of b with extremes at zero and unity and with an average of $^1/_2$. For $b > b_c$, on the other hand, P_{ex} drops rapidly to zero with increasing b.

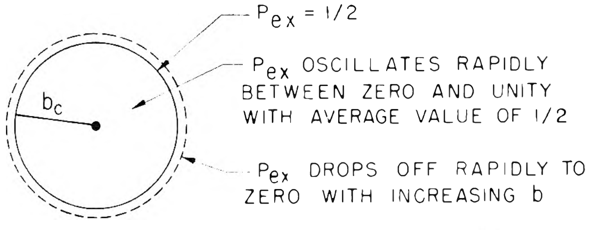


Fig. 3.—Charge exchange in atom–ion collision.

In view of this situation we may take $(1 - \cos\theta)$ equal to unity for $b < b_c$, and may then write (4) as

$$Q_M = \pi b_c^2 + \int_{b_c}^{\infty} (1 - \cos\theta) 2\pi b \, db$$

Again anticipating results to be obtained below, we may remark that the first of the two terms of the right-hand side of (5) gives by far the largest contribution to Q_M. The second term contains the effects of the residual small charge-exchange for $b > b_c$ plus the bona-fide scattering without charge-exchange; the latter is due essentially to the so-called "polarization" component of the atom-ion interaction energy, and turns out to be quite small ($\sim$1%). The crucial importance of charge-exchange in momentum transfer between ions and parent gas atoms is thus established.

We now come to the problem of computing the charge-exchange probability, P_{ex}, as a function of impact parameter, b. This computation can readily be carried out once the atom–ion interaction is known. Figure 4 gives this interaction for the case of helium. For the sake of comparison the mean thermal energy of relative motion, $3kT/2$, for T at room temperature (20°) is also given.

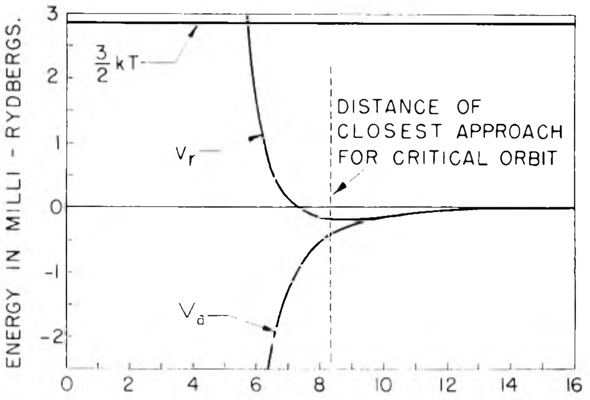


Fig. 4.—Atom–ion interaction for helium.

The ion–atom interaction consists of two terms. The first, predominant at large internuclear distances (> 9 Bohr radii, in the case of He) is the "polarization" interaction between the ion and the induced dipole moment of the neutral atom. It has the form $-C/r^4$, where r = internuclear separation, $C = e^2\alpha/2$, and α is the atomic polarizability; the latter quantity may be obtained either theoretically or from measurements of the dielectric constant of the gas.[3] The second term, the so-called "charge-exchange" or "resonance" interaction, actually consists of two branches, as shown in Fig. 4. This feature is connected with the degeneracy remarked above in which, to the first order, the energy of the system does not depend upon which of the atoms A or B is ionized; in the language of quantum mechanics, the two states, ψ_A and ψ_B, in which atoms A and B are ionized, respectively, are degenerate with regard to the "unperturbed" energy. This degeneracy is removed by the interaction between A and B, thus splitting the electronic energy of the system into two branches. It is characteristic that in this, as well as other cases of degeneracy removal, the states corresponding to the two branches are not ψ_A and ψ_B, but linear combinations of these. In fact, the states ψ_r and ψ_a associated with the repulsive and attractive branches of Fig. 4 are

$$\psi_r = 2^{-1/2} [\psi_A - \psi_B] \exp\left[-\int^t iE_r dt/h\right]$$

$$\psi_a = 2^{-1/2} [\psi_A + \psi_B] \exp\left[-\int^t iE_a dt/h\right] \qquad (5)$$

In (5) the time-dependence of ψ_r and ψ_a is written out explicitly, the functions ψ_A and ψ_B being taken

---

[3] Higher order corrections, such as terms in $1/r^6$ (van der Waals interactions) are negligible at internuclear distances of significance in our problem.

time-independent. Also

$$E_r = E_0 + V_r$$
$$E_a = E_0 + V_a \qquad (6)$$

where E_0 is the degenerate unperturbed level and V_r, V_a the repulsive and attractive potential energy curves of Fig. 4 (inclusive of the polarization term). V_r and V_a are, of course, functions of time *via* the time dependence of the internuclear separation.

It should be pointed out that the combinations $\psi_A \pm \psi_B$ are just those which occur in the theory of the molecular ion formed by the colliding ion and atom. In the case of helium, for example, ψ_a and ψ_r are the two lowest electronic states of He_2^+: ${}^2\Sigma_u$ and ${}^2\Sigma_g$; similar considerations apply to other gases.

In the problem at hand, however, as contrasted with the situation commonly encountered in molecular physics, the state of our diatomic system is not stationary, *i.e.*, it is neither ψ_a nor ψ_r, but rather a linear superposition of them. It is this feature which, as we shall show immediately below, is intimately involved in the theory of charge-exchange between an ion and its parent atom.

We choose a time t_i sufficiently early so that A and B may be considered as non-interacting. (t_i will later be allowed to regress to $-\infty$). At t_i the state of the system is one in which either A or B is ionized. Choosing for the sake of definiteness the former, we then have, using (5)

$$\psi(t_i) = \psi_A \equiv C_r\psi_r(t) + C_a\psi_a(t) \qquad (7)$$

where

$$C_r = 2^{-1/2} \exp\left[i\int^{t_i} E_r\, dt/h\right]$$
$$C_a = 2^{-1/2} \exp\left[i\int^{t_i} E_a\, dt/h\right] \qquad (8)$$

Substituting (5) into (8), we then obtain, after a little algebra, the result, valid for arbitrary t,

$$\psi(t) = \exp\left[-i\int_{ti}^{t}(E_r + E_a)\, dt/2h\right]$$
$$\times \left\{ \psi_A \cos\left[\int_{t_i}^{t}(E_r - E_a)dt/2h\right] + \right.$$
$$\left. i\psi_B \sin\left[\int_{t_i}^{t}(E_r - E_a)dt/2h\right]\right\} \qquad (9)$$

We now introduce a time t_f sufficiently later than the encounter between A and B so that the atoms may be considered as no longer interacting. (t_f may, in fact, be taken positively infinite.) The probability of charge-exchange during the collision is then equal to the absolute square of the coefficient of ψ_B in (9) at time t_f. Passing to the limit $t_i \to -\infty$ and $t_f \to +\infty$, we obtain

$$P_{ex} = \sin^2\left[\int_{-\infty}^{+\infty}(E_r - E_a)dt/2h\right]$$

or

$$P_{ex} = \sin^2\left[\int_{-\infty}^{+\infty}(V_r - V_a)dt/2h\right] \qquad (10)$$

In order to make further progress, we require knowledge of $V_r - V_a$ as well as of the classical orbit of relative motion. With regard to the former, a brief discussion will be given below, a complete treatment being reserved for a later paper.[4] For our present purposes V_r and V_a may be represented by the formulas

$$V_r = -c/r^4 + V_1 e^{-\alpha r}$$
$$V_a = -c/r^4 - V_1 e^{-\alpha r} \qquad (11)$$

where V_1 and α are suitably chosen constants for each gas. With regard to orders-of-magnitude, these are indicated in Fig. 4; for the internuclear separations with which we shall be concerned (> 8 Bohr radii in the case of He) both V_r and V_a are small compared to $3kT/2$ when T is room temperature. This feature indicates the feasibility of using, as a first approximation, the simplest type of classical orbit, namely, straight-line trajectories. These are characterized analytically by the expression

$$r = (b^2 + v^2t^2)^{1/2} \qquad (12)$$

where v is the relative velocity of the colliding ion-atom pair. (12) incorporates the dependence on impact-parameter which will ultimately appear in P_{ex}.

We now insert (12) into (10); under the condition that $\alpha b >> 1$ (a condition which is always fulfilled in practice), the integral can be evaluated approximately; one obtains

$$P_{ex} = \sin^2\left[\frac{V_1 e^{-\alpha b}}{hv}\left(\frac{2\pi b}{\alpha}\right)^{1/2}\right] \qquad (13)$$

We observe

(1) b_c is defined implicitly by the equation

$$\frac{\pi}{4} = \frac{V_1 e^{-\alpha b_c}}{hv}\left(\frac{2\pi b_c}{\alpha}\right)^{1/2} \qquad (14)$$

(2) With decreasing b the phase of P_{ex} increases exponentially; P_{ex} thus oscillates rapidly between zero and unity for $b < b_c$. A detailed argument, not presented here, shows that, except in the immediate neighborhood of b_c, the average value of P_{ex} is $1/2$.

(3) For $b > b_c$, $P_{ex} \cong (2\pi\, bV_1^2/\alpha hv^2)e^{-2\alpha b}$ which diminishes rapidly with increasing b.

It will be remembered that these properties were utilized earlier in this paper to demonstrate the importance of charge-exchange for momentum transfer between ions and parent atoms.

We may here remark that, in the case of helium, b_c turns out to be of the order of 8 Bohr radii. For other gases, b_c is even greater. The effective "collision radius" is thus seen to be large compared to atomic dimensions. In particular, it is definitely larger than the radius for momentum transfer between an ion and a foreign-gas atom, in which charge-exchange plays no significant role.

Referring back to (5), we may estimate the magnitude of the second term of that equation under the assumption that actual deflections for $b > b_c$ are negligible and that the whole effect arises from charge-exchange. In this case, it is easily shown that

$$\int_{b_c}^{\infty}(1 - \cos\theta)\, 2\pi\, bdb = \int_{b_c}^{\infty} 4\pi P_{ex} bdb \cong \pi b_c/\alpha \qquad (15)$$

roughly a 10% correction in specific cases.

---

(4) To be published in *The Physical Review*. In this paper we shall treat the nuclear motion quantum mechanically and thereby provide the formal justification for the semi-classical approach of the present paper.

The contribution to Q_M of true scattering—deflection of the ions by the atoms without charge-exchange—has been estimated for specific cases and turns out to be small ($\sim 1\%$).

Up to the present we have not taken into account the polarization component of the ion–atom interaction. The primary effect of this component is a modification of the orbit of relative motion so that (12) is no longer valid. In particular, the distance of closest approach, $r_{\min}$, is less than b; it is given implicitly by the relation

$$b^2/r_{\min}^2 = 1 + c/Er_{\min}^4 \qquad (16)$$

E being the kinetic energy of relative motion as defined at the beginning of this paper. It then turns out that one obtains substantially the right result by replacing b by $r_{\min}$ in (14). In practical cases the effect of this replacement on Q_M is of the order of 10%.

Equations (5), (14), (15), (16), and the above paragraph provide the recipe for obtaining Q_M as a function of E once the constants V_1 and α, which characterize the resonance interaction, are known. The determination of this interaction is nothing more than the problem of calculating electron-energy curves of diatomic molecular ions at large internuclear separations. For the case of helium, V_r and V_a have been computed by Massey and Mohr[5] utilizing a perturbation treatment based on the approximation of electronic wave functions by combinations of atomic orbitals. (The simplest calculation of this type, that for H_2^+, is given in standard texts.[6]) In our treatment, we have employed an alternate method which we believe provides more accurate results at the large internuclear separations of interest in the mobility problem. A complete description of this method will appear in a later paper.[4] We give below a very brief summary for the simplest possible case: the interaction of a proton with a hydrogen atom, *i.e.*, the H_2^+ problem.

Referring to Fig. 5, we note that the Hamiltonian of the electron is unchanged by reflection of the electron coördinates through the median plane, M, which bisects the internuclear axis. From this symmetry feature it follows that either the wave function, ψ, or its normal derivative, $d\psi/dn$, vanish on M. This condition permits us to formulate the problem as follows: Solve Schrödinger's equation in a half-space, *e.g.*, region I of Fig. 5, with the boundary conditions, $\psi = 0$ or $d\psi/dn = 0$ on M and the regularity of ψ at infinity. The solution in region II is then obtained by reflection through M; in this operation ψ either changes sign or does not, depending on whether ψ or $d\psi/dn$ is equal to zero on M.

The (ground-state) hydrogen wave-function differs from the solution of this problem in two respects. Firstly, the potential energy is that due solely to proton A, whereas the potential in our problem is that arising from both protons. Secondarily, the hydrogen wave-function does not satisfy either of the boundary conditions $\psi = 0$ or $d\psi/dn = 0$ on M.

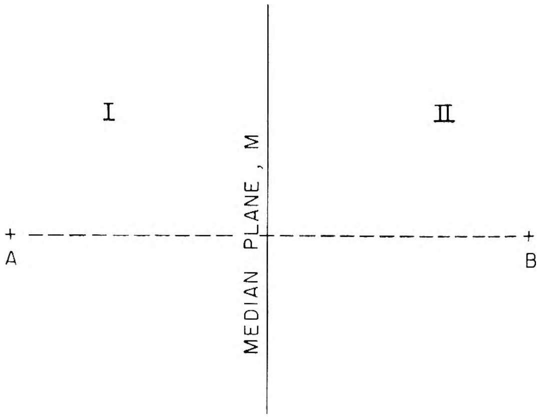


Fig. 5.—The H_2^+ problem. The median plane, M, bisecting the internuclear axis, divides space into two regions. Since ψ is either an even or odd function with respect to reflection through M, it is sufficient to solve the problem, *e.g.*, in region I, where the potential of proton B may be regarded as a small perturbation.

The first deficiency may be remedied by a generalized W.K.B. method[7] which treats the effect of proton B in region I as a perturbation. It then turns out that the difference between the corrected wave-function and the zero'th-order hydrogen wave-function, although insignificant in the immediate neighborhood of proton A, becomes appreciable in the neighborhood of the median plane. It is this feature which, in our opinion, constitutes the chief weakness of the atomic-orbital method. Specifically, combinations of atomic orbitals do not provide accurate molecular orbitals in those regions which contribute importantly to the integrals of the conventional perturbation treatment.

After having corrected for the presence of the second proton, one has to introduce further adjustments both in the wave-function and in the energy eigenvalue, to satisfy one of the two admissible boundary conditions on M. This is done by a special perturbation procedure which lack of space prevents us from describing here.

The adjustment in energy eigenvalue required to satisfy the conditions on M is precisely the quantity being sought, namely, the first approximation to the electronic energy as a function of internuclear separation. The result in the case of hydrogen is, approximately

$$V = -C/r^4 \pm (\pi r/2)(4/\epsilon)e^{-r}$$

where r is expressed in Bohr radii and where the plus and minus signs hold for the boundary conditions on M, $\psi = 0$ and $d\psi/dn = 0$, respectively.

The method outlined above for the case of hydrogen may be applied to atoms whose outermost shell is an s-shell. For the computation, knowledge of the behavior of the s-wave-function at large distances from the atomic core is primarily all that is required. This knowledge is obtained from Hartree-type calculations, from which it is usually possible to express the *normalized* atomic wave-function at large distances from the atomic core in the form

$$\psi(\rho) \approx Ne^{-Ze\rho}$$

---

(5) H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc.* (*London*), **144**, 188 (1934).

(6) *E.g.*, H. A. Bethe, *Handbuch Physik*, **24**, 1, Chapter 3, pp. 528–529.

(7) For a standard presentation of the W.K.B. method see, for example, L. I. Schiff, "Quantum Mechanics," first edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

where N and Z_e are suitably chosen constants. One then has, for the electronic energy, the expression

$$V = -C/r^4 \pm (\pi r N^2/2)\,(4/e)^{1/Z_e} e^{-Z_e r}$$

This expression is not altogether of the form of equation (11) because of the presence of the factor r in the resonance term. However, over a limited region of interatomic separation—and this is all that is required for the computation of P_{ex}—this factor can be approximated by a suitable exponential. As pointed out above, once the resonance interaction is known, one can proceed straightforwardly to a determination of Q_M as a function of E. Inserting the results into equation (1) and (2) we may then compute the ionic mobility.

Specific calculations have been carried out for neon and argon. The results are $K = 4.2$ and 1.64 cm./sec. per volt/cm., respectively, under conditions of standard gas density (2.69×10^{19}/cc.) and $T = 293$°K. We remark here that neon and argon were chosen specifically for the purpose of comparison with the recent measurements of Hornbeck[8]; from the theoretical standpoint, the choice is not too advantageous since the outer shells of both these elements are p-shells, rather than s-shells, as required by our theory. The calculations therefore entailed further approximations, in addition to those already introduced in the theory. However, it is estimated that the errors therewith incurred do not exceed 10%.

DISCUSSION

R. M. NOYES (Columbia University).—Is not mobility reduced by charge transfer because the cross section is so much greater than the gas viscosity cross section? It would seem that if charge transfer occurred only when the particles are as close as the gas viscosity collision diameter, charge transfer should not affect the mobility.

T. HOLSTEIN.—It is true that, if the charge transfer took place only within the gas viscosity collision diameter, its effect on mobility would be negligible. In the case of ion-atom collisions, however, there exists the additional polarization interaction whose effective collision diameter is larger than that for ordinary gas viscosity. It is this diameter which must be exceeded by the diameter for charge-exchange in order for the latter to be significant.

H. RIES (Bell Lab.).—In connection with Professor Franck's question concerning the fact that H^+ in H_2O achieves a higher mobility through charge transfer while in gaseous conductivity the mobility is reduced by transfer, I would like to point out that in the gas the transferred particle only carries the charge at the moment of its transfer. This means in the case of long free paths that the carrier is not mainly the exchanged particle. The effect of transfer is to produce larger deflections and so reduce mobility. In the case of H^+ in H_2O the H_2O molecules do very little moving and the exchanged particle, *i.e.*, H^+, is the principal carrier. Hence, here, the transfer phenomenon leads to greater mobility.

K. RUEDENBERG (University of Chicago).—The author reports a new method for computing the energy of the H_2^+ ion at large internuclear distances. I would like to raise the following points: 1. What would be the closest internuclear distance when this approximation is still valid? Would it have any bearing on molecular structure calculations? 2. It is well known that wave functions of a rather simple analytical form [Such solutions have been given by James and by Svartholm.] reproduce Hylleraas' result for the H_2^+-energy up to about 5 significant figures. It seems possible that these energy curves might give an even simpler solution than the one given by Dr. Holstein.

T. HOLSTEIN.—1. The internuclear distance in question is of the order of 5 Bohr radii. Since this distance is large compared to the usual interatomic distances in molecules, the applicability of the approximation to molecular structure calculations is rather dubious.

2. The quoted papers [H. M. James, *J. Chem. Phys.*, **3**, 9 (1935); N. Svartholm, *Z. Physik*, **111**, 186 (1938–39)] claim only to have reproduced Hylleraas' result for H^+_2 in the neighborhood of the energy minimum (~2 Bohr radii). No results have been obtained for large internuclear separations; in fact James states [*loc. cit.*, p. 14] that his wave function is "of course, not so well adapted to the treatment of molecules for very large separations of the nuclei."

---

(8) J. A. Hornbeck, *Phys. Rev.*, **84**, 615 (1951).

THE MEASUREMENT OF ELECTRON EXCHANGE IN GASES AT LOW PRESSURE[1]

BY E. E. MUSCHLITZ, JR., AND J. H. SIMONS
College of Engineering, University of Florida, Gainesville, Florida

Received March 15, 1952

The basis for the method for experimental determination of electron exchange in the gaseous phase is discussed with particular details given for the apparatus used by Simons and co-workers. Recent experimental results are compared. An explanation for the abnormally large probabilities observed for electron exchange between positive ions and large polyatomic molecules is put forward. A brief summary of the importance of the electron exchange phenomenon is given.

Two types of inelastic collisions may be distinguished. The first type includes those collisions in which kinetic energy is converted into excitation energy. Ionization and excitation by electron impact are examples of this type. The second type is the converse of the first. In this case, excitation energy of one of the colliding particles is converted into kinetic energy, or is transferred in the form of excitation to the second particle.[2] Examples of such collisions are given in Table I, where E_e, E_d and E_i are energies of excitation, dissociation and ionization, respectively. A positive value of ΔE means that some of the kinetic energy of the colliding particles must be used in order for the process to take place, while a negative value means that excess energy in the process is converted into kinetic energy. In general, a process is the more probable, the smaller the absolute value of ΔE.[3]

TABLE I

COLLISIONS OF THE SECOND KIND

(1)	$A^* + B \longrightarrow A + B^*$	$\Delta E = E_e(B) - E_e(A)$
(2)	$A^* + B \longrightarrow A + B$	$\Delta E = -E_e(A)$
(3)	$A^* + B_2 \longrightarrow B + B + A$	$\Delta E = E_d(B_2) - E_e(A)$
(4)	$A^+ + B \longrightarrow A + B^+$	$\Delta E = E_i(B) - E_i(A)$
(5)	$A^+ + A \longrightarrow A + A^+$	$\Delta E = 0$
(6)	$A^+ + B_2 \longrightarrow A + B_2^{+*}$	$\Delta E = E_i(B_2) + E_e(B_2^+) - E_i(A)$
(7)	$A_2^+ + B_2 \longrightarrow A_2^* + B_2^+$	$\Delta E = E_i(B_2) + E_e(A_2) - E_i(A_2)$

The first three equations in the table represent reactions which have been studied extensively in photochemical investigations. Equation (1) is an example of sensitized fluorescence; (2) and (3) are examples of the quenching of fluorescence. Equations (4)–(7) are examples of electron exchange processes in which a positive ion is neutralized on collision with an atom or molecule. As a result, a new positive ion is produced. It should be noted that Eq. (4) is entirely analogous to (1). In the following discussion, electron exchange collisions in the gaseous phase will be considered.

The electron exchange process was discovered simultaneously in 1927 by Smyth[4] and Harnwell and by Hogness and Lunn. Early investigations of the phenomenon were made by Kallmann and Rosen,[5] Rostagni[6] and Wolf.[7] It was realized at an early stage that the new ions formed had very small kinetic energies compared to the 10–1,000 ev. energies of the primary ions used; *i.e.*, the process takes place with very little exchange of kinetic energy. This fact provided a basis for quantitative measurements of probabilities or cross-sections for the process.

Method of Measurement

All of the experimental work to date is based on the following principles. Consider a monoenergetic well-defined, beam of ions passing through a gas. Both elastic and inelastic collisions reduce the intensity of the beam, but if the intensity (or beam current), I, is measured at two points a distance l apart along the beam path, a total cross-section α_T, may be calculated using the absorption equation, Eq. (8). Here, α_T is the total absorption cross-section in units

$$I_1 = I_0 e^{-\alpha_T l p} \qquad (8)$$

of cm.^{2} per cm.^{3} of gas at one mm. pressure and 0°. In terms of the total cross-section for the average individual collision in cm.^{2}, σ_T, $\alpha_T = 3.536 \times 10^{16} \sigma_T$. In order that Eq. (8) be valid, the pressure must be low enough for the mean free path of the primary ions to be several times larger than l. If this is the case, secondary collisions can be neglected. Furthermore, if the current, I_N, due to the slow ions formed by the electron exchange process along l can be separately measured, a cross-section, α_N, for the process may be calculated from the equation

$$\frac{\alpha_N}{\alpha_T} = \frac{I_N}{I_0 - I_1} \qquad (9)$$

since $I_0 - I_1$ is equal to the current lost from the beam as a result of both charge exchange and elastic scattering. The cross-section for elastic scattering, α_S, is then obtained by subtracting α_N from α_T. At high primary ion energies (greater than 100 ev.) other inelastic processes become important, particularly the ionization process

$$A^+ + B \longrightarrow A^+ + B^+ + e^- \qquad (10)$$

In this process, slow ions are produced which are not the result of electron exchange, hence additional difficulties are encountered.

In nearly all of the work that has been done, the secondary ion current is measured on a separate electrode placed adjacent to the beam. A small negative voltage on this electrode serves to pull out all of these slow ions without appreciably affecting the ion beam or the elastically scattered ions. Elastic scattering through large angles will interfere, but for ions of energies greater than 10 ev. very little elastic scattering occurs through angles greater than 20°. Much of the early work is open to question, since the necessary conditions for quantitative measurements were not achieved.

Simons and co-workers began an investigation of the elastic scattering of hydrogen ions in gases in 1937–1938. In their first paper it was noted that the effect of electron exchange would have to be taken into consideration quantitatively before precise measurements of elastic scattering

---

(1) Assistance in writing this paper from the Office of Naval Research, Physics Branch, is gratefully acknowledged.

(2) O. Klein and S. Rosseland, *Z. Physik*, **4**, 46 (1921); J. Franck, *ibid.*, **9**, 259 (1922).

(3) J. Franck, *Naturwissenschaften*, **14**, 211 (1926).

(4) H. D. Smyth, G. P. Harnwell, T. R. Hogness and E. G. Lunn, *Nature*, **119**, 85 (1927).

(5) H. Kallmann and B. Rosen, *Z. Physik*, **61**, 61 (1930); *ibid.*, **64**, 806 (1930).

(6) A. Rostagni, *Nuovo Cim.*, **12**, 134 (1935).

(7) F. Wolf, *Ann. Phys.*, **29**, 33 (1937); *ibid.*, **30**, 313 (1937).

could be obtained.[8] With this end in view the apparatus described below was constructed. A complete description may be found elsewhere.[9]

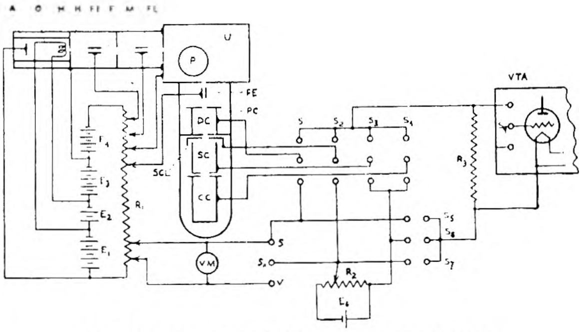


Fig. 1.—Simplified diagram of apparatus.

A simplified diagram of this apparatus is shown in Fig. 1. Positive ions produced in a hydrogen glow discharge pass through a hole in the cathode, K, into the chamber, F, where they are electrostatically focused into M and U. In U, the H^+, H_2^+ and H_3^+ ions of which the beam consists are separated magnetically. The homogeneous ion beam passing into the chamber, PC, is refocused, and finally collimated by the two holes at the top and bottom of the defining cylinder, DC. The chamber, O, is operated with about 1.5 mm. hydrogen pressure, while chambers, F, M, U and PC are pumped out continually by four separate, high speed, mercury vapor pumps. Details of the focusing system in F and M are shown in Fig. 2. The focusing elements are $^1/_4''$ cylinders arranged coaxially.

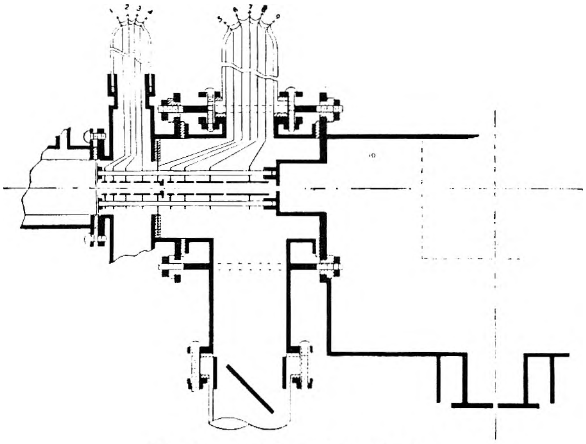


Fig. 2.—Ion focusing system.

Figure 3 shows the details of the chamber, PC, and the analysis chamber below it. A diaphragm having a hole in the center separates these two regions. The ion beam passes through this hole into the cylinder, SC. The gas under investigation is allowed to leak continually into the analysis chamber, so that an equilibrium pressure of 10^{-2} to 10^{-4} mm. is obtained. A hole in the bottom of SC limits the ions which are collected by the cylinder, CC, to those which have undergone little or no deflection in passing through the gas. Ions which have been elastically scattered through larger angles, and ions formed by electron exchange are collected on SC or on the separately insulated cover, SCL. If electron exchange is taking place, a small retarding potential applied between SCL and SC will draw the slow ions up to SCL. This is demonstrated in Fig. 4, in which $R_N = I_N/I_0$ is plotted against the retarding potential for the three hydrogen ions in water vapor.[10] Very little rise in R_N is observed for H_3^+, and it is therefore evident that the inelastic process is not a very probable one in this case. However, for the other two ions, a sharp rise is observed, and the curve is essentially horizontal for retarding potentials greater than 3 volts. The ions drawn to SCL must therefore have very small energies.

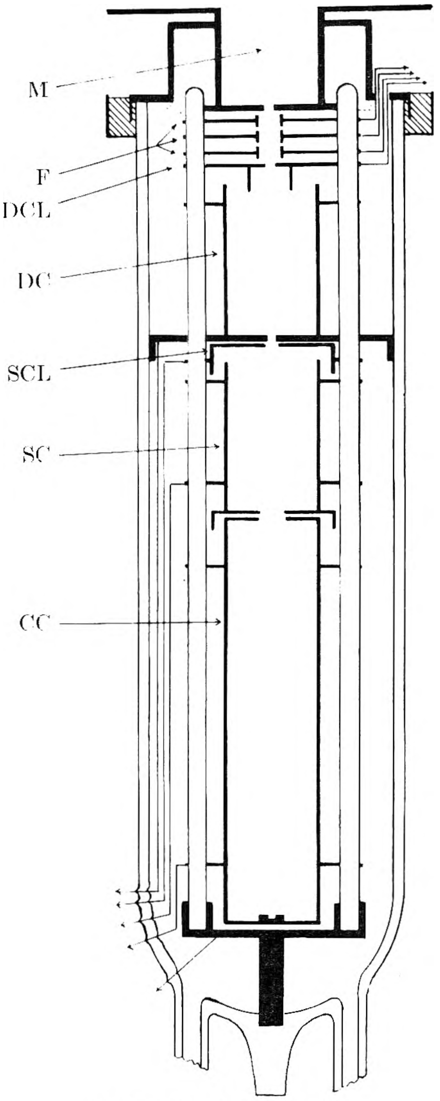


Fig. 3. Analysis chamber.

In the investigations carried out with this apparatus, both scattering and electron exchange cross-sections were calculated from the currents to SCL, SC and CC, measured both with and without the retarding potential, using equations[11] related to Eq. (8) and (9). The energy range investigated was 5–150 ev. In most cases electron exchange data were taken below 10 ev., but the cross-sections thereby obtained are not considered reliable, because of large angle elastic scattering and distortion of the ion beam by the retarding potential.

One of the limiting factors in any investigation of molecular collisions is the measurement of pressure. This is particularly true when non-permanent gases are used. A modified Knudsen gage[12] of high precision was therefore constructed for use with the apparatus described above.

Experimental Results

Representative data are shown in Figs. 5–8, in which cross-sections are plotted against incident ion energy.

---

(8) A. S. Russell, C. M. Fontana and J. H. Simons, *J. Chem. Phys.*, **9**, 381 (1941).

(9) J. H. Simons, H. T. Francis, C. M. Fontana and S. R. Jackson, *Rev. Sci. Instruments*, **13**, 419 (1942).

(10) J. H. Simons, H. T. Francis, E. E. Muschlitz, Jr., and G. C. Fryburg, *J. Chem. Phys.*, **11**, 316 (1943).

(11) J. H. Simons, C. M. Fontana, H. T. Francis and L. G. Unger, *ibid.*, **11**, 312 (1943).

(12) G. C. Fryburg and J. H. Simons, *Rev. Sci. Instruments*, **20**, 541 (1949).

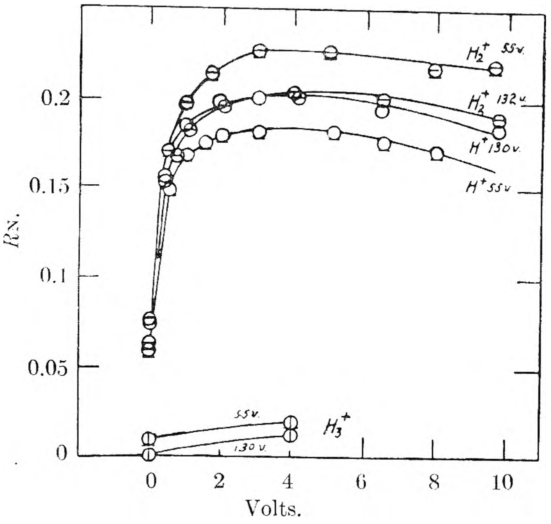
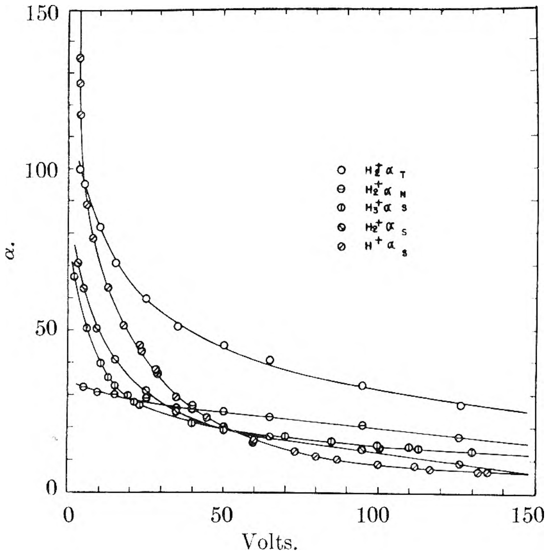


Fig. 4.—Analysis of ions formed by the electron exchange process.

Protons and H_3^+ are not neutralized to any appreciable extent in hydrogen in the energy range investigated (Fig. 5). Electron exchange does take place for H_2^+ in H_2, giving an abnormally large total cross-section. The electron exchange cross-section increases slowly with decreasing energy and seems to approach a finite value at zero energy. The neutralization of He^+ ions in He (Fig. 9) and A^+ ions in argon shows a similar behavior.[13]



Scattering of hydrogen ions in hydrogen

Fig. 5.—Scattering and neutralization of hydrogen ions in hydrogen.

All three hydrogen ions undergo neutralization in the hydrocarbon gases. Figures 6 and 7 show data taken for protons in methane[14] and ethane.[15] The electron exchange cross-sections shown are typical of all the hydrocarbons investigated insofar as they are very large, and increase with decrease in incident ion energy. The neutralization of protons in methane, for example, accounts for about 70% of the total cross-section, even in the very low energy range.

Figure 8 shows data for H_3^+ in methane. The electron exchange cross-section is much smaller than that for protons in methane. Relatively small cross-sections for the neutralization of H_3^+ were found for all the hydrocarbons investigated.

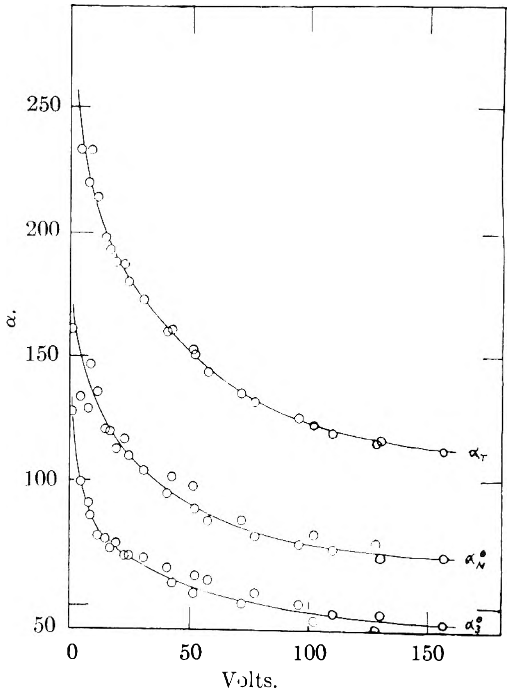


Fig. 6.—Scattering and neutralization of protons in methane.

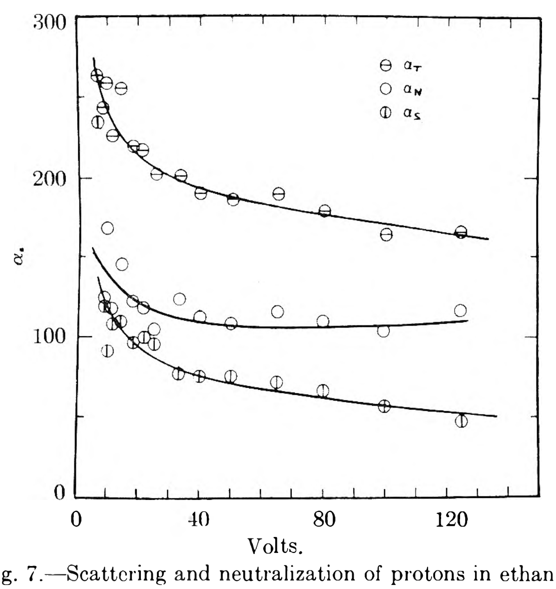


Fig. 7.—Scattering and neutralization of protons in ethane.

A summary of the available data for 100 ev. protons is given in Table II. The difference between the ionization potentials of the hydrogen atom (13.60 ev.) and the gas molecule is listed in the last column. The gases are listed in the order of their ionization potentials. The electron exchange cross-sections above ethane fit the qualitative prediction of quantum theory.[16,17] For a given ion velocity, the probability of electron exchange will increase to a maximum as $\Delta E = E_i(H) - E_i(B)$ approaches zero. The expected maximum would lie between krypton and methane.

The electron exchange cross-sections for ethane and the remaining hydrocarbons are very large despite the large values of ΔE. Although these data are not as precise as for methane and hydrogen, it does not seem conceivable that the experimental error in these cases could be more than ±10%. In the second column of Table II, elastic scattering cross-sections are listed for the gases investigated by Simons

---

(13) J. B. Hasted, *Proc. Roy. Soc.* (*London*), **A205**, 421 (1951).

(14) J. H. Simons and G. C. Fryburg, *J. Chem. Phys.*, **13**, 216 (1945).

(15) J. H. Simons and S. A. McAllister, in process of publication.

(16) P. M. Morse and E. C. G. Stückelberg, *Ann. Phys.*, **9**, 579 (1931).

(17) H. S. W. Massey and R. A. Smith, *Proc. Roy. Soc.* (*London*), **A142**, 142 (1933).

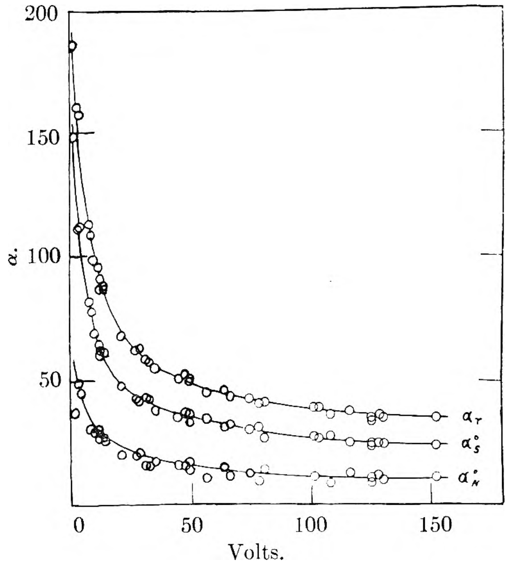


Fig. 8.—Scattering and neutralization of H_3^+ in methane.

and co-workers. Hasted[13] did not make determinations of the elastic scattering. These cross-sections increase in a very reasonable fashion with the size of the molecule. This gives support to the belief that the α_N values are correct, since α_S is obtained by a difference method which involves α_N.

Table II

Electron Exchange and Elastic Scattering Cross-Sections for 100 ev. Protons

Gas (B)	α_S	α_N	Ref.	$E_i(B) - E_i(H)$[18]
He	3.3	<0.1	19	+10.88
A	. . .	1.5	13	+ 2.17
H_2	9.3	<0.5	20	+ 1.83
Kr	. . .	48	13	+ 0.41
CH_4	47	77	14	− 0.56
H_2O	34	51	10	− 0.99
Xe	. . .	28	13	− 1.44
C_2H_6	58	112	15	− 1.82
C_3H_8	80	130	15	− 2.30
n-C_4H_{10}	117	114	21	− 2.49
i-C_4H_{10}	203	71	21	− 2.54
C_2H_4	49	82	22	− 2.98
C_3H_6	61	144	22	− 3.55

An explanation of these large electron exchange cross-sections may well lie in the fact that these molecules and the molecular ions derived from them can absorb considerable vibrational energy. If a process, such as Eq. (6) in Table I, is taking place, the energy which must be converted into kinetic energy in the process is reduced by the vibrational, and perhaps rotational, energy given to the new ion formed. Since a large number of vibrational and rotational states are available, the effective value of ΔE for the process can be very small, thereby leading to a large electron exchange cross-section.

A process such as

$$H^+ + C_2H_6 \longrightarrow H^* + C_2H_6^+ \qquad (11)$$

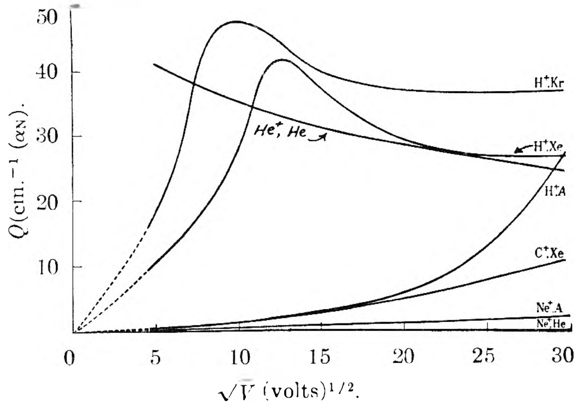


Fig. 9.—Electron exchange cross-sections.

would not provide a similar explanation, insofar as the first excited state of $H(2^2P_{1/2})$ is 10.15 ev. above the ground state, giving ΔE for Eq. (11) as +8.33 ev. The additional possibility of this type of process, however, complicates any interpretation of electron exchange data for molecular ions as distinguished from atomic ions. Equation (7) of Table I illustrates such a process. In this case, the excited molecule formed may have electronic as well as vibrational–rotational excitation. In an electron exchange collision between a molecular ion and a polyatomic molecule, both the new ion and new molecule formed may therefore have energy of excitation after the collision. There is an even greater chance in this case that the energy which must be converted into kinetic energy in the process will be very small.

Recent theoretical work[23,13] indicates that the electron exchange cross-section, at least for atomic ions in monatomic gases, should pass through a maximum for

$$a\Delta E/hv \sim 1 \qquad (12)$$

where a is a length of the order of the atomic dimensions involved, ΔE is the difference in ionization energies, and v is the velocity of the incident ions. A maximum is found for protons in xenon and krypton by Hasted.[13] Some of his work is shown in Fig. 9. That a similar behavior has not been found for the neutralization of hydrogen ions in water vapor or hydrocarbon gases may again be due to the fact that the effective ΔE is very small, and hence a maximum will be obtained only at an extremely low ion velocity. The remaining data in Fig. 9, with the exception of the symmetrical case, He^+ in He, show an increase in the cross-section with increasing energy. The large negative value for ΔE in these cases would put the maximum beyond the range of the measurements.

Recent measurements of electron exchange cross-sections have been made in the high energy range (> 1000 ev.) by Keene[24] for protons and helium ions. At these energies, however, the ionization process is a much more probable one than electron exchange.

Importance of the Electron Exchange Phenomenon

(1) Production of Beams of Fast Atoms and Molecules.—Early investigators[25] recognized the possibility of utilizing electron exchange as a means of producing fast beams of atoms and molecules. This technique has been used successfully by Amdur, *et al.*,[26] in their determinations of collision cross-sections for fast atoms. The molecular beam

---

(18) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948); J. J. Mitchell and F. F. Coleman, *ibid.*, **17**, 44 (1949).

(19) J. H. Simons, E. E. Muschlitz, Jr., and L. G. Unger, *ibid.*, **11** 322 (1943).

(20) J. H. Simons, C. M. Fontana, E. E. Muschlitz, Jr., and S. R. Jackson, *ibid.*, **11**, 307 (1943).

(21) J. H. Simons and W. H. Cramer, *ibid.*, **18**, 473 (1950).

(22) J. H. Simons and L. G. Unger, *ibid.*, **13**, 221 (1945).

(23) H. S. W. Massey, *Rep. Prog. Phys.*, **12**, 248 (1949).

(24) J. P. Keene, *Phil. Mag.*, **40**, 369 (1949)

(25) H. Kallmann and B. Rosen, *Naturwissenschaften*, **18**, 867 (1930).

(26) I. Amdur and H. Pearlman, *J. Chem. Phys.*, **8**, 7 (1940); I. Amdur, M. C. Kells and D. E. Davenport, *ibid.*, **18**, 1676 (1950).

method has in the past proved to be a powerful tool in the investigation of the fundamental properties of nuclei, atoms and molecules. The above technique for the production of such beams has important advantages over the oven method. A beam that is homogeneous in velocity is obtained, rather than one with a Maxwellian distribution of velocities. Using this technique, beams consisting of molecular fragments or molecular species that are unstable under ordinary conditions may be produced. A study of the neutralization of the H_3^+ ion, for example, may well provide an experimental approach to the problem of the stability of the triatomic hydrogen molecule.

(2) **Gaseous Discharges and Transport Phenomena.**—Electron exchange between ions and molecules is an important process in gaseous discharges, second only to the ionization and recombination processes. At the low pressure of the upper atmosphere, electron exchange would be a more probable process than recombination. The symmetrical charge transfer process in certain cases is the limiting factor governing the mobility of positive ions in gases.[27] In measurements of ion mobilities, small impurities have a considerable effect on the results. If electron exchange takes place between the ion under investigation and molecules present as a small impurity, the resulting mobility observed will be partly due to the new ions, since a large number of collisions are involved.[28]

(3) **Chemical Reactions.**—The electron exchange process may be important in the mechanism of many chemical reactions. In flames and explosions, for example, ions are present, so that this process may have particular importance. If the ions play a role in the reaction mechanism, then the occurrence of electron exchange between the ions and neighboring gas molecules would need to be given consideration in elucidating the mechanism.

(4) **Atomic and Molecular Structure.**—As the electron exchange phenomenon is a fundamental process involving atoms and molecules, studies both experimental and theoretical of this phenomenon will contribute significantly to our knowledge of atomic and molecular structure.

In conclusion, the possibility of electron exchange between a negative ion and a neutral molecule might be mentioned. No evidence for such a process has yet been found, yet there seems to be no reason that it should not take place. In addition, there appears to be no evidence to prohibit an analogous phenomenon, that of proton exchange in the gaseous phase. Such a phenomenon has long been postulated in solutions. In the electrical conductance of acid solutions, for example, the proton may be considered to move from one water molecule to the next in this fashion.

DISCUSSION

RAY I. POTTER (National Bureau of Standards).—Have you used different path lengths for the ion beam?

E. E. MUSCHLITZ, JR.—No. We have, of course, made measurements as a function of pressure for the same path length in order to determine whether the pressure was low enough to insure single collisions of the positive ions. The electron exchange phenomenon is such a highly probable process in the case of the hydrocarbons that elastically scattered ions undergo neutralization to an appreciable extent before they reach the surface of SC, even at pressures as low as 1×10^{-4} mm.[14] This difficulty was overcome by extrapolating the results for the hydrocarbons to zero pressure.

RAY I. POTTER (National Bureau of Standards).—Have you made measurements that could be compared with those of Hasted?

MUSCHLITZ.—No. Our interest in this work, until recently, has mainly been in the measurement of the elastic scattering cross-sections as a function of ion energy, from which the attractive force law between the ion and the neutral molecule could be evaluated. The recent work on the hydrocarbons was done in order that a comparison might be made of the attraction for protons of these molecules. The construction of an improved apparatus for the measurement of electron exchange is being planned. If this apparatus is built, we will doubtless repeat some of our own measurements of electron exchange, as well as those of Hasted.

ROBERT L. PLATZMAN (Purdue University).—This comment concerns the suggestion of Muschlitz and Simons in explanation of the apparent result that impact of a positive ion and a *polyatomic* molecule may have a particularly great effective cross section for electron capture by the ion. The mechanism—participation in the energy balance of some oscillational quanta in such a way as to decrease the "energy defect" (energy which must be transformed from electronic energy of a molecule to kinetic energy of a heavy particle, or *vice versa*)—has been proposed and examined in a paper by Professor Franck and myself which is now in course of publication (J. Franck and R. Platzman, "Physical Principles Underlying Photochemical and Radiation-Chemical Reactions," Volume I, Chapter II, Section 4.3a in "Radiation Biology," McGraw-Hill Book Co., New York, N. Y., 1953), and I have also considered its possible influence in capture-and-loss phenomena of *very swiftly moving* ions. (Another simple manifestation of the molecular properties underlying this reasoning is the conclusion that, in the "fast" collision of A and A^+, exact resonance, and very great cross section for electron exchange, occurs only if A is monatomic: identical molecules, one of them an ion, are not in exact resonance, because the equilibrium nuclear separations of ionized and neutral molecules are in general different.) It should be emphasized, however, that a much more penetrating analysis than has yet been given, involving both further experimental and theoretical study and exploring the other factors which one knows must cause the cross section to vary from molecule to molecule, is required before this effect can be considered to have been established. It should also be borne in mind that the shorter is the "collision time," the more the Franck–Condon principle restricts the latitude in this "energy-balancing" process.

MUSCHLITZ.—We agree that a more penetrating analysis of this problem is necessary before a conclusion can be safely reached. From the experimental standpoint, it might be pointed out that a great deal could be learned from an energy analysis of the slow ions produced in the neutralization process. In the case of proton scattering in the hydrocarbons, for example, it should not be difficult to determine whether the hydrocarbon ions have thermal or nearly thermal energies, or whether they have several electron volts kinetic energy. We propose to modify the apparatus in future work so that this might be done.

---

[27] H. S. W. Massey and R. A. Smith, *Proc. Roy. Soc.* (*London*), **A142**, 142 (1933).

[28] A. M. Tyndall and C. F. Powell, *ibid.*, **A129**, 162 (1930).

CHARGE TRANSFER IN THE RADIATION CHEMISTRY OF GASES[1,2]

BY MILTON BURTON AND JOHN L. MAGEE

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

Received March 16, 1952

Charge and excitation transfers play important roles in radiation chemistry, the mechanism of which can be examined most clearly for gases. In such transfer, complex formation is involved. Ion clusters so produced involve bonds of typical strength running up to 2 ev. or more. A simplified calculation of their lives is described. The lifetimes in typical cases may be of the order of seconds. In such time, charge neutralization, internal conversion, chemical dissociation and chemical reaction (including aggregation or polymerization) with other molecules may be important competing processes. For excitation transfer, the method of calculation of lives of complexes is formally the same but there are important quantitative differences. One important conclusion is that, in the radiation chemistry of gases, both ionization and excitation processes (including transfer) are significant. An apparent exception to this conclusion, the polymerization of acetylene vapor, is examined and an explanation consistent with these views is offered.

1. Introduction

In the radiation chemistry of liquid mixtures of certain hydrocarbons, transfer of both ionization and excitation from primarily affected molecules to other molecules apparently plays an important role in the over-all chemistry observed.[3,4] Similarly, in dilute solutions of a variety of potentially fluorescent solutes in benzene, absorption of incident high-energy radiation (*e.g.*, X-rays) is predominantly by the benzene while the fluorescence is characteristic of the solute.[5] There is also evidence that benzene and other aromatic hydrocarbons may photosensitize the decomposition of alkyl iodides in liquid solution.[6] In addition, existence of mercury-sensitized reactions in the liquid state is also known.[7] However, only a limited number of such liquid systems has been studied. Although there have been statements as to the conditions under which energy transfer and radiosensitization (and correlated protection) may appear in the liquid state,[3,4] no indications of the theoretical limitations on such transfer have been expressed.

The gaseous systems whose radiation chemistry and photochemistry have been so far studied are somewhat more susceptible to theoretical analysis. The significance of non-adiabatic transitions in such cases has been fairly well examined[8,9] and the mechanism of simple photosensitized reactions now seems to be understood.[8] In particular, for photosensitization it is both established and understood that the existence of adequate energy in the photosensitizing molecule is of itself an insufficient criterion for prediction of a photosensitization process[10]; a mechanism for the energy transfer must exist. For radio sensitization there must be similar requirements. The formal similarities between photochemistry and radiation chemistry have been emphasized, but actually the most important energy transfer processes may be significantly different. By contrast to excitation transfer, the theory of charge transfer and its effects in the radiation chemistry of large molecules have not been carefully examined.

Evidence for charge transfer in radiation chemistry was first shown by Lind and his co-workers,[11] who employed the term "ionic catalysis" with a clear understanding of its special meaning. In particular he showed that in a number of radiolyses and radiation-induced polymerizations rare gases were effective "ionic catalysts." Such "ionic catalysis" is possibly exhibited by acetylene, which seems to radiosensitize decomposition of benzene.[12] Eyring[13] has suggested a valence-bonding mechanism for this effect and points out that "catalysis" may be possible even when charge transfer is not.[14] On the other hand, carbon dioxide does not radiosensitize the oxidation of methane or carbon monoxide in spite of a favorable ionization potential relationship.[11]

Evidently, limitations on probability of charge transfer in gaseous mixtures are significant in radiation chemistry. Such limitations are, of course, only to be understood in terms of the detailed mechanisms of the individual processes, and each case of interest must be examined separately. In rare gas collisions and in most cases so far discussed in this Symposium, the binding energy between the colliding partners is low and collisions last about 10^{-13} sec. In collisions between polyatomic ions and molecules, the factors of possible increased binding energy and consequent greater life of the collision complex are especially significant. In such cases, we must consider, as is not uncommon in kinetics, the effect of "sticky collisions"; *i.e.*, collisions whose half-lives are long compared with 10^{-13} sec.

2. Theory

2.1 Sticky Collisions between Ions and Molecules.—A collision between an isolated pair of

---

[1] Paper presented at the Symposium on Electron Transfer and Isotopic Reactions under the joint auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society and the Division of Chemical Physics of the American Physical Society at the University of Notre Dame, June 11, 1952.

[2] Contribution from the Radiation Project, operated by the University of Notre Dame and supported in part under Atomic Energy Commission contract AT(11-1)-38.

[3] J. P. Manion and M. Burton, THIS JOURNAL, **56**, 560 (1952).

[4] S. Gordon and M. Burton, *Discussion Faraday Soc.*, **12**, in press (1952).

[5] H. Kallmann and M. Furst, *Phys. Rev.*, **79**, 857 (1950); **81**, 853 (1951).

[6] W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932); W. West and W. E. Miller, *J. Chem. Phys.*, **8**, 849 (1940).

[7] M. K. Phibbs and B. de B. Darwent, *ibid.*, **18**, 679 (1950).

[8] K. J. Laidler and K. Shuler, *Chem. Revs.*, **48**, 153 (1951). Many literature references are given here.

[9] J. L. Magee, THIS JOURNAL, **56**, 555 (1952).

[10] *Cf.* J. T. Dubois and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 1512 (1951).

[11] *Cf.* S. C. Lind, "The Chemical Effect of Alpha Particles and Electrons," 2nd Ed., Chemical Catalog Co. (Reinhold Publ. Corp.), New York, pp. 184 *et seq.*

[12] C. Rosenblum, THIS JOURNAL, **52**, 474 (1948).

[13] H. Eyring, *J. Chem. Phys.*, **7**, 792 (1939).

[14] *Cf.* R. J. Munson and K. Hoselitz, *Proc. Roy. Soc.* (*London*), **A172**, 43 (1939), who found evidence for the reaction $Li^+ + Xe \rightarrow LiXe^+$. Li has a smaller ionization potential than Xe.

atoms cannot be "sticky" since there is no degree of freedom which can interchange energy with relative-motion energy. The only requirement for sticky collisions is that degrees of freedom exist which can exchange energy with the energy of relative motion of a colliding pair; thus any polyatomic system might have such collisions. The quantitative features of this situation are best discussed from the point of view of the inverse process, *i.e.*, the dissociation. We ask the question: What is the lifetime of a complex which exists in an associated state but which has sufficient energy to dissociate? A rigorous solution to this problem in quantum mechanics would require knowledge of all bound states of the associated system and their interaction with states which lead to dissociation. The solution in classical mechanics is somewhat more simple in principle; there are no restrictions on energy transfer between vibrational degrees of freedom and only the potential function of the system is required. In a treatment similar to that of the absolute reaction rate theory one can calculate the rate at which a randomly distributed ensemble (microcanonical ensemble) of systems passes through a potential-energy saddle point leading to dissociation.[15,16]

A simplified form of the expression for the lifetime of a complex derived by this method is

$$\tau = \nu^{-1}\left(1 - \frac{E_B}{E}\right)^{1-\alpha}$$

where E is the actual energy of the system in relative energy, E_B is the binding energy of the two entities which form the complex, α is the number of vibrational degrees of freedom of the complex, and ν is a constant having dimensions of frequency and being of the order of magnitude of a molecular vibration frequency.

In cases of interest to us here, E will be approximately equal to $E_B + kT$, and so we can also write

$$\tau \approx 10^{-13}\left(\frac{E_B + kT}{kT}\right)^{\alpha-1}$$

This treatment, although by no means rigorous, gives us a good qualitative insight into the situation. Long lifetime for a given collision complex is favored by large binding energy E_B and by many degrees of freedom, α. In a rare gas collision for example, $\alpha = 1$, and so

$$\tau = 10^{-13}$$

according to the formula, regardless of E_B.

Table I gives some values of τ as a function of the two significant parameters. Apparently, long lifetimes can be expected for complexes which have only moderate values of E_B, if α is 6 or so.

TABLE I

SOME COMPLEX LIFETIMES IN SECONDS (E_B IS IN ELECTRON VOLTS)

E_B	$\alpha - 1$ 3	 6	 9	 12
0.25	1.33×10^{-10}	1.77×10^{-7}	2.35×10^{-4}	3.13×10^{-1}
0.5	9.25×10^{-10}	8.55×10^{-6}	7.90×10^{-2}	
0.75	2.98×10^{-9}	8.83×10^{-5}	2.63×10^{-1}	
1	6.88×10^{-9}	4.73×10^{-4}		
2	5.32×10^{-8}	2.83×10^{-2}		
3	1.77×10^{-7}	3.13×10^{-1}		

2.1.1 Competing Processes.—Clearly, only relative times required for various competing processes, not absolute lifetimes, usually concern us. For example, in a gas at atmospheric pressure a complex which lives 10^{-10} sec. will be stabilized by a collision and remains associated. Also, for ions, there is always a neutralization reaction and frequently a possible internal conversion to another state, *e.g.*, a charge transfer process.

An important competing process, of general interest, which in many cases terminates the existence of the complex is electron capture. Indeed, it appears from Table I that unless an intermediate chemical change occurs, neutralization would precede ordinary dissociation of the ion complex in most cases of interest. Where the lives of the complexes are relatively short (*e.g.*, only slightly greater than time between collisions), collisions will tend to stabilize the complexes and to preserve them for neutralization of chemical charge.

2.1.2 Values of Parameters.—Values of E_B are positive for the interaction of an ion with any polyatomic molecule, because of polarization interaction with the latter. If, in addition, the molecule is strongly dipolar, the value of E_B may be several electron volts because of classical coulombic interactions alone. Furthermore, as Eyring[13] has pointed out, an ion is chemically unsaturated; thus, states with attractive exchange interaction result.

The value of α to use in a given case is somewhat uncertain. If an attempt is made to allow for quantum restrictions on energy transfer by taking an "effective" value of α, we see that α must be $3N - 6$ or less where N is the total number of atoms in the complex. For complexes with high symmetry and stiff vibrations α could be considerably less than $3N - 6$.

2.1.3 Cluster Sizes.—Ample experimental evidence exists for complexing of ions in gases.[17-19] A particularly striking illustration of long lifetimes of ionic collision complexes involves the case of rare gas ions in water vapor (in which clusters may include six molecules of water[18]). Clusters are shown to grow when the probability for a single three-body collision is so small as to rule out a three-body process for formation of the first bond. A typical value of E_B would be 2 ev. and the maximum value of α would be 9. Thus, a lifetime even of the first pair could easily be of the order of one second.

Later we discuss the case of acetylene plus rare gas ions, in which little can be said of the value of E_B. However, acetylene has chemical unsaturation in addition to a moderate polarizability and slightly polar C–H bonds. It would seem highly probable that the value of E_B is considerably

---

(15) J. L. Magee, to be published.

(16) *Cf.* G. E. Kimball, *J. Chem. Phys.*, **5**, 310 (1937), for a more specialized treatment of this problem applied to association of radicals.

(17) L. B. Loeb, "Fundamental Processes of Electrical Discharge in Gases," John Wiley and Sons, Inc., New York, N. Y., 1939, p. 38 ff.

(18) A. M. Tyndall, "Mobility of Positive Ions in Gases," Cambridge University Press, Cambridge, 1938.

(19) Diatomic ions of the rare gases have recently been observed by J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951). These molecular ions can be formed by bimolecular collisions $He^* + He \rightarrow He_2^+ + e$ between excited and normal atoms. The analogous process for excited molecules has not been discussed.

greater than kT for at least one state, and the value of α could be as large as 12. Thus highly sticky collisions are anticipated.

2.2 Mechanism of Excitation Transfer.—Formally, excitation transfer is a process similar to charge transfer[9]; *i.e.*, it is an internal conversion in a collision complex. The lives of the complexes may be handled by the treatment just outlined. There are quantitative differences (*e.g.*, binding energies are probably lower on the average) but the important competing processes are not greatly modified. The specific rate of production of excited complexes is decreased relative to that of production of ion complexes by the fact that in the latter case coulomb fields extend collision diameters. On the other hand, the neutralization process important for ionic complexes may be supplanted in an excited complex by light emission. The probability of light emission is a fixed characteristic of the complex whereas that of neutralization depends on the rate of irradiation. In both cases, the complexes may have ample time to be terminated by chemical reaction. Thus, we see that irradiation rate and activation energies, particularly for rearrangement processes, play a special, complicated role. In general, we may expect both excitation and ionization transfer to play an important part in the chemical effects observed, but their relative importance is not *a priori* established in any general way.

2.3 Some Conclusions.—Several conclusions derive from this theoretical analysis. (1) In the radiation chemistry of gaseous mixtures both ionization (*i.e.*, charge) transfer and excitation transfer may play a significant role. (2) In general, specific mechanisms for such transfer are required; mere adequacy of energy relationships is insufficient. (3) No apparent reason exists for an expectation of significant difference in *a priori* probability of the two different types of transfer in the gaseous state. (4) The need for a special mechanism of ionization transfer involving what, in kinetics, is generally called a "sticky collision" bears a formal resemblance to one aspect of the ion-cluster theory of radiation chemistry proposed by Lind and indicates that clustering, even though transitory, may have real importance. On the other hand, it cannot be pretended that the present theory of radiation chemistry is thus reconciled to the old theory. In particular, the present theory places no special weight on ionization, ionization transfer, and sticky collisions involving ions; excitation and excited molecules play a parallel role. Any case in radiation chemistry which purports to show a special role of ions and ionization thus merits and requires detailed consideration.

3. Comment on Radiation-Polymerization of Acetylene

In a critical examination of the present status of the theory of radiation chemistry, Lind[20] has presented the data shown in Table II. This case is particularly interesting for two reasons. The constancy of the calculated values of M/N, or molecules of acetylene converted to cuprene per calculated ion-pair produced, for a number of added inert gases in a considerable range of concentration indicates ionization as the only potent precursor of chemical change in the acetylene. The same constancy indicates that this potency is independent of the nature of the entity primarily ionized, whether it be reactant or inert additive. Table II shows that each of the inert additives has ionization potential greater than that of acetylene (I = 11.41 ev.). It might be thought that the initial ionization whether it be primarily in the additive or in the acetylene would quickly end up in the latter and produce therein the effect that might be expected in pure acetylene. The difficulty, as Lind has noted, is that according to present views[21] we might also expect excitation to play a significant role, at least in the pure acetylene. Lind has rightfully stated that these results must be clearly explained if the present theory of radiation chemistry (*i.e.*, that all classes of excited molecules may be the precursors of reaction) is to be held acceptable.

TABLE II

SUMMARY OF ACETYLENE SITUATION ACCORDING TO LIND[a]: DATA ON α-PARTICLE-INDUCED POLYMERIZATION

Added inert gas	E_α	I	$E_\alpha - I$	E_α/I	M/N
None					19.8
He	27.8	24.581	3.2	1.13	19.7
Ne	27.4	21.559	5.8	1.27	19.2
N_2	35.0	15.576	19.4	2.24	18.5
A	25.4	15.756	9.6	1.61	18.2
Kr	22.8	13.996	8.8	1.63	19.6
Xe	20.8	12.127	8.7	1.72	18.0

[a] We are indebted to Dean S. C. Lind for the use of this table in advance of publication. E_α is the energy required per ion pair and I is the ionization potential. Presumably $E_\alpha - I$ is energy which has gone into excitation.

The paradox in the acetylene situation is that photochemically-induced polymerization of acetylene has been observed. The quantum yield for the process at an average wave length of 2150 Å. (*i.e.*, corresponding to 5.7 ev.) is 9.2 ± 1.5 molecules of acetylene converted to a product resembling cuprene per photon absorbed.[22] The temperature coefficient, 1.25 over a 10° interval, suggests a rate-controlling reaction of low activation energy (*i.e.*, ~4 kcal.). The limited evidence available[23] is consistent with the view that in the photochemical case the chain is begun by excited acetylene and propagated by an excited aggregate.

To understand the results of radiation chemistry in the light of this apparently contradictory evidence we must flatly conclude that excited states of acetylene, such as can be primarily produced in number exceeding the number of ionized states, are ineffective in production of polymerization in the presence of ions. Possible processes by which

---

[20] S. C. Lind, Paper presented at the XIIth International Congress of Pure and Applied Chemistry, New York City, September 12, 1951.

[21] M. Burton, *J. Chem. Ed.*, **28**, 404 (1951).

[22] S. C. Lind and R. L. Livingston, *J. Am. Chem. Soc.*, **52**, 4613 (1930); **54**, 94 (1932).

[23] *Cf.* G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, New York, 1939, p. 350; W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, 1941, p. 332.

such an effect can be achieved divide into two classes: either a specially effective mechanism for deactivation of excited molecules exists in presence of ions, or in a system containing ions (and polymer ions) the excited acetylene molecules are chemically removed without effective contribution to the total number of acetylene molecules polymerized. The second alternative seems more reasonable. It remains only to see whether a general form of mechanism for such a process, consistent with our present chemical theory, can be suggested.

Without straying too far from the purposes of this paper and without undue speculation we may note that an excited state of acetylene must survive sufficiently long for formation of the first complex, that this state may be a metastable one resultant from the initial excited state, and that this state must interact far more readily with ions than with the relatively large concentration of unexcited molecules. Evidently, for clarification of this mechanism additional work on polymerization of acetylene, particularly on the combined effect of ultraviolet light and high-energy radiation, is required.

DISCUSSION

NORMAN DAVIDSON (Cal. Tech.).—I think that the formula for the lifetime of the complex

$$\tau \approx 10^{-13}\left[\frac{E_B + kT}{kT}\right]^{\alpha-1}$$

is incorrect. It should be

$$\tau \approx 10^{-13}\left[\frac{E_B + (s+1)kT}{(s+1)kT}\right]^{\alpha-1}$$

The quantity skT is the average vibrational energy in the two components of the complex before association. This correction decreases the calculated lifetimes. E_B is the ΔE_0^0 for the formation of the complex from its components. This remark does not invalidate the main point of the paper, *i.e.*, that such complexes have a good chance of being stabilized by collision before they dissociate, and they will then persist to take part in other reactions.

J. L. MAGEE.—Professor Davidson is correct in his observation that the energy E of the complex is not exactly equal to $E_B + kT$. In fact E is the average energy of the complex in its α vibrational degrees of freedom. For complexes which are formed in collisions of non-linear polyatomic molecules and ions, five of these vibrational degrees of freedom arise from rotational states of the components and one from relative translational motion. Thus for this case

$$E = E_B + 3kT + skT$$

where skT is the total average vibrational energy of the original components and the $3kT$ is the average energy in the five rotational states and the one translational state. A complex which is formed from a linear molecule (*e.g.*, acetylene) and a rare gas ion has two vibrations which were formed from a translational and rotational degree of freedom respectively and the others arise from the vibrations of the molecule. In this case

$$E = E_B + kT + skT$$

We see that in any case the approximation we have used is rough and the results of the calculation can only be considered as illustrative. It should be noted, however, that values of s are not as great as the total number of vibrational degrees of freedom of the colliding molecules. Acetylene, for example, at room temperature has s approximately *unity*.

THE EXCHANGE REACTION BETWEEN THE TWO OXIDATION STATES OF IRON IN ACID SOLUTION[1]

BY JOSEPH SILVERMAN[2] AND R. W. DODSON

Chemistry Department, Columbia University, New York, N. Y., and Brookhaven National Laboratory, Upton, N. Y.

Received March 13, 1952

The rate of exchange between ferrous and ferric iron in perchloric and hydrochloric acid solutions has been measured at ionic strength 0.55 f, at temperatures from 0 to 20°. The reaction is first order in the over-all concentration of each oxidation state. The rate increases with decreasing acid concentration and with increasing chloride concentration. The results suggest four reaction paths involving ferrous ion, namely, with: (1) unhydrolyzed ferric ion, Fe^{+++}, (2) $FeOH^{++}$, (3) $FeCl^{++}$ and (4) $FeCl_2^{+}$. The specific rate constants at 0° are 0.87, 1.0×10^3, 9.7 and about 15 f^{-1} sec.$^{-1}$, respectively, for these reaction paths. The corresponding experimental activation energies are 9.9, 7.4, 8.8 and about 10 kcal./mole, respectively. The rate increases with ionic strength. No evidence was found for a specific perchlorate ion effect.

Introduction

The exchange reaction between ferrous and ferric iron in 3 f perchloric acid solution has been the subject of several investigations. Nahinsky,[3] employing a chemical method to separate the exchanging species, reported the exchange to be complete in five seconds. Van Alten and Rice[4] used a diffusion technique to separate the reacting species in order to avoid catalysis which might be induced by a chemical separation. They observed a half-time of 18.5 ± 2.5 days. This latter work also yielded the rather unexpected result that ferric iron diffused twice as rapidly as the ferrous species. Linnenbom and Wahl[5] repeated the Van Alten–Rice experiment but obtained entirely different results. They found that the half-time was less than two hours and that ferrous iron diffused 40 ± 20% faster than the ferric iron. Kierstead[6] also performed this same experiment. He reported half-times of 39 ± 2 days and 166 ± 12 days, and stated that the ferrous iron diffused three to four times faster than the ferric iron. Betts, Gilmour and Leigh,[7] using the diffusion separation method, found that the exchange was complete in one-half hour and that the ferrous iron diffused 22 ± 4% faster than the ferric iron. A chemical separation recently devised[8] has yielded half-times of the order of seconds for the exchange reaction.

The present work presents a study of the kinetics of the reaction, made through the use of a modification of this separation. The data obtained confirm the preliminary experiments,[8] and are consistent with the results of Linnenbom and Wahl, of Betts, Gilmour and Leigh, and of Nahinsky. However, they are in complete disagreement with the results of Van Alten and Rice, and of Kierstead.

In the experiments reported below, the rate of the exchange reaction has been determined as a function of ferrous and ferric concentrations, acid concentration, chloride concentration and temperature. The effect of various neutral salts was also observed.

Materials.—A ferric perchlorate stock solution was prepared from a hydrochloric acid solution of high specific activity Fe^{55}, obtained from the U. S. Atomic Energy Commission, Oak Ridge, Tennessee. This nuclide decays by K capture with a 2.94 year half-life[9] emitting 5.9 kev. manganese X-rays. The radioactive iron was extracted into isopropyl ether by a standard method[10] to free it from metal contaminants, and was then back-extracted into water. In order to convert this to a ferric perchlorate solution of desired concentration and specific activity, additional inactive iron was required. Iron wire, obtained from the General Chemical Co., was dissolved in nitric acid and oxidized to the ferric state with hydrogen peroxide. After the excess peroxide had been destroyed by prolonged boiling, the solution was mixed with the purified radioactive iron solution and then made alkaline with ammonia. After several cycles of solution with perchloric acid, precipitation with ammonia, and washing with water, the washings gave negative tests for chloride, sulfate and ammonium ions. The purified ferric hydroxide was then dissolved in a calculated volume of standardized perchloric acid to produce a stock solution of 0.00110 f ferric perchlorate in 0.0507 f perchloric acid. This solution also gave negative tests for chloride and sulfate ions.

A master stock solution of ferrous perchlorate was prepared by successive recrystallizations of ferrous perchlorate hexahydrate (obtained from the G. Frederick Smith Co.) from 8 f perchloric acid. The resulting solution was about 0.3 f in ferrous perchlorate and about 2 f in perchloric acid. It gave a negative test for sulfate ion but was about 0.004 f in ferric perchlorate and about 5×10^{-5} f in chloride ion. An aliquot of the solution was analyzed for ferrous ion by titration with standard ceric sulfate. Another aliquot was passed through a Jones reductor and titrated with ceric sulfate to give the total iron concentration. A third aliquot was treated with hydrogen peroxide to oxidize all the iron to the ferric state. After the excess peroxide was boiled off, the hot sample was titrated to the phenolphthalein end-point with standard sodium hydroxide, thus precipitating all the iron as ferric hydroxide and neutralizing all the acid.[11] The perchloric acid concentration was determined from this titer after taking account of the hydroxide used up in precipitating the iron and that produced during the oxidation process. A stock solution containing 0.0011 f ferrous perchlorate, 1.5×10^{-5} f ferric perchlorate, and less than 10^{-6} f chloride ion was periodically prepared from the master solution. Each time such a solution was prepared, the master solution was re-analyzed. Both stock solutions of ferrous perchlorate were stored at about −5° in order to minimize the oxidation of the ferrous iron to the ferric state by dissolved oxygen and perchlorate ion.

Sodium perchlorate solutions were made up from the monohydrate, obtained from the Eimer and Amend Co. These solutions gave negative tests for chloride and sulfate ions. Salt concentrations were determined by specific gravity measurement.

Perchloric acid (70% vacuum distilled), purchased from J. T. Baker Chemical Co., was standardized by titration

---

(1) This work was carried out at Brookhaven National Laboratory under the auspices of the United States Atomic Energy Commission.

(2) Now at Walter Kidde Nuclear Laboratories, Inc., New York, N. Y.

(3) Ph.D. Thesis, University of California, 1942.

(4) L. Van Alten and C. N. Rice, *J. Am. Chem. Soc.*, **70**, 883 (1948).

(5) V. J. Linnenbom and A. C. Wahl, *ibid.*, **71**, 2589 (1949).

(6) H. A. Kierstead, *J. Chem. Phys.*, **18**, 756 (1950).

(7) R. H. Betts, H. S. A. Gilmour and K. Leigh, *J. Am. Chem. Soc.*, **72**, 4978 (1950).

(8) R. W. Dodson, *ibid.*, **72**, 3315 (1950).

(9) G. L. Brownell and C. J. Maletskos, *Phys. Rev.*, **80**, 1103 (1950).

(10) R. W. Dodson, G. J. Forney and E. H. Swift, *J. Am. Chem. Soc.*, **58**, 2573 (1936).

(11) W. C. Schumb and S. B. Sweetser, *ibid.*, **57**, 871 (1935), describe this method of titrating acid solutions of ferric iron.

with standard sodium hydroxide. It gave negative tests for chloride and sulfate.

Constant boiling hydrochloric acid, whose concentration was also checked by titration with standard sodium hydroxide, was the source of the hydrochloric acid solutions employed in the experiments described below.

A solution containing 0.05 *f* perchloric acid and 0.025 *f* α,α'-dipyridyl was prepared. The latter was obtained from Eastman Kodak and Eimer and Amend.

Lanthanum oxide was obtained from the Varlacoid Co. A spectrographic analysis detected 0.001% praseodymium as the only metal impurity. The oxide was heated to 1000° for a few hours; after cooling it was treated with slightly less than an equivalent amount of perchloric acid. The filtered solution was 1.91 *f* in lanthanum perchlorate. The lanthanum concentration was determined by precipitating the hydroxide from a 50% alcohol solution and then filtering, igniting and weighing the precipitate. The solution gave a negative test for chloride ion but proved to have a $9 \times 10^{-4} f$ sulfate ion content as determined by the barium sulfate gravimetric method.[12]

All other chemicals employed were standard chemically pure reagents.

Experimental Procedure

The ferric fraction of the reaction mixture was prepared by the addition of appropriate volumes of the stock solutions to a wide-mouthed amber reagent jar (about 400-ml. capacity), which also served as the reaction vessel. The ferrous fraction was prepared in a 125-ml. erlenmeyer flask. The concentrations of the two fractions in a particular run were nearly identical with respect to all components except for ferrous and ferric iron. This precaution minimized heat and volume effects which might accompany mixing.

Both fractions were brought to constant temperature (±0.1°) in a thermostatically-controlled bath. The reaction was started by rapidly pouring the ferrous fraction into the reaction vessel. During the mixing process, the contents of the reaction vessel were stirred by a motor-driven glass propeller. Aliquots of the reaction mixture were withdrawn at measured time intervals. Each aliquot was transferred to a 100-ml. beaker and the reaction was immediately quenched by the rapid successive addition of 10 ml. of the dipyridyl stock solution and enough sodium acetate solution to bring the *p*H to about 5. The function of the dipyridyl is to render the ferrous iron inert to exchange processes by formation, rapid at this *p*H, of the highly stable, intensely red ferrous tris-α,α'-dipyridyl ion.[13]

The two iron species were then separated by precipitation of the ferric iron. In the absence of lanthanum salts, ferric hydroxide was precipitated with ammonia. When lanthanum was present, the precipitation was performed with 8-hydroxyquinoline. Because of the low reactant concentrations employed, an aliquot of an inactive ferric perchlorate solution was added following the precipitation to increase the mass of the precipitate. Also an aliquot of a fine supension of diatomaceous earth (Johns–Manville Super-Cel) was added to aid the filtration. The amount of diatomaceous earth added to each sample was such that it took a 15% variation in this amount to produce a 1% change in the self-absorption of the radiation emitted by the precipitate.

The precipitates were filtered on Whatman number 42 paper, washed, dried, mounted on cards, and covered with cellophane squares. Most of the samples were counted with end-window Geiger tubes connected to standard scalers. Some runs were counted on a sensitive proportional counter designed for X-ray counting.[14] With this instrument set so as to count only the K lines of manganese, the data confirmed the results obtained with the Geiger counter.

In one experiment, performed in the study of the chloride dependence, the ferrous fraction was also counted. The filtrates from the ferric iron filtration were acidified with hydrochloric acid and boiled until they turned colorless. Bromine water was added to oxidize the iron to the ferric state. Counting samples were then prepared from the resulting solutions in a manner identical with that described above for the ferric iron.

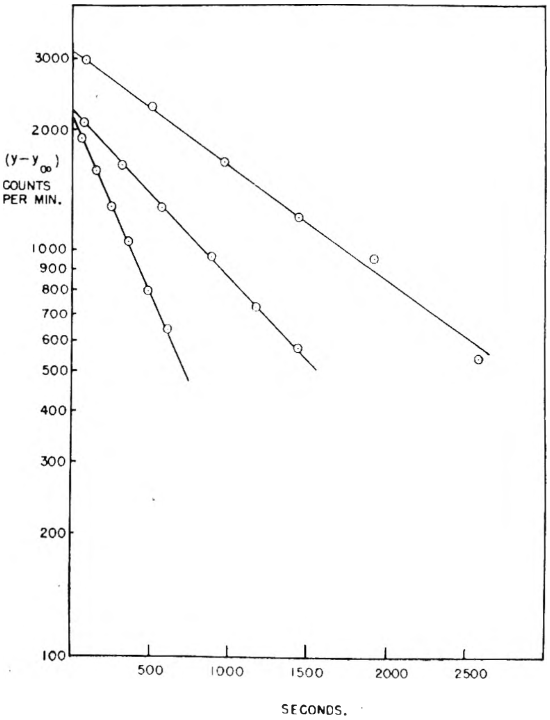


Fig. 1.—Typical rate data.

During each run, eight aliquots were analyzed. The first six were withdrawn before four half-lives had elapsed. The last two were infinite time samples, which were withdrawn after a lapse of at least ten half-lives. In cases where oxidation of ferrous iron was expected to provide complications, the seventh was removed after the passage of ten half-lives and the eighth was removed after at least fifteen half-lives. The pairs of infinite time samples usually agreed within about 3%.

Results

Order of the Reaction.—The order of the reaction was determined by independent variations of the concentrations of the reactants. If there are no slow consecutive reactions and the concentrations of the reactants do not vary with time, the time dependence of the fraction of activity exchanged is given by the rate law[15]

$$\ln \frac{y - y_\infty}{y_0 - y_\infty} = -R\,\frac{(a + b)}{ab}\,t \qquad (1)$$

where y_0, y and y_∞ represent the specific activities of the initially active material at zero time, time t, and infinite time, respectively. R is the constant rate at which the over-all exchange process occurs, and a and b are the gross concentrations of the two reactants. Representative experimental curves of $\ln(y - y_\infty)$ *versus* t are shown in Fig. 1. The fact that these plots are straight lines, in agreement with the properties of equation (1), indicates that the assumptions involved in the derivation of this equation apply to the systems under consideration.

The rate law may also be expressed by a similar equation which describes the growth of activity with time in the initially inactive material

$$\ln(1 - x/x_\infty) = -R\,\frac{(a + b)}{ab}\,t \qquad (2)$$

where x and x_∞ represent the specific activity of the initially inactive material at time t and infinite time. In the instance where the ferrous fraction was analyzed, a plot of $\ln(1 - x/x_\infty)$ *versus* t yielded the anticipated linear relationship.

Values of the exchange rate R were computed from the half-time of plots such as those in Fig. 1. It has been shown[16] that incomplete separation or partial catalysis of

---

[12] E. H. Swift, "A System of Chemical Analysis," Prentice-Hall Publishers, Inc., New York, N. Y., 1939, p. 478.

[13] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55, 736 (1950), have made equilibrium and kinetic studies of this ion.

[14] W. Bernstein, H. G. Brewer, Jr., and W. Rubinson, *Nucleonics*, **6**, 39 (1950).

[15] (a) H. A. C. McKay, *Nature*, **142**, 997 (1938); (b) R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).

[16] R. Prestwood and A. Wahl, *ibid.*, **71**, 3137 (1949).

TABLE I

DETERMINATION OF THE ORDER OF THE EXCHANGE REACTION AT 0.0°

$(HClO_4)$, f	(HCl), f	(Fe^{III}), $f \times 10^4$	(Fe^{II}), $f \times 10^4$	$t_{1/2}$, sec.	k, f^{-1} sec.$^{-1}$	α	β
0.547	$<5 \times 10^{-6}$	1.03	0.998	2540	1.34	1.00 ± 0.05	
		1.05	1.97	1670	1.38		
		1.06	2.94	1315	1.31		
		1.08	3.92	1045	1.33		
		2.10	3.94	850	1.35		1.00 ± 0.05
		3.11	3.95	730	1.34		
		4.24	3.85	638	1.34		
		4.18	3.92	606	1.41		
0.0508	$<5 \times 10^{-6}$	1.07	3.09	273	6.10	1.00 ± 0.05	
		1.06	2.06	368	6.03		
		1.05	1.03	568	6.07		1.00 ± 0.05
		2.09	2.06	267	6.25		
		3.13	2.06	231	5.78		
0.0385	0.509	1.11	4.10	279	4.77	1.00 ± 0.05	
		1.07	2.05	477	4.65		
		1.05	1.03	691	4.82		
		2.15	4.10	224	4.95		1.00 ± 0.05
		3.18	4.10	196	4.86		

an exchange reaction by the separation method does not affect the value of R determined in this way provided these effects are reproducible in each run. In our experiments the apparent zero time exchange, *i.e.*, the value of 100 x/x_∞ at time zero, averaged about 35%.

If R has a simple power dependence upon a and b, one can write

$$R = ka^{\alpha}b^{\beta} \qquad (3)$$

where k is the specific reaction rate constant, and α and β represent the reaction order with respect to a and b, respectively. The dependence of $t_{1/2}$ upon the concentration of ferrous and ferric iron was determined in three different media: 0.547 f perchloric acid, a mixture of 0.0508 f perchloric acid and 0.496 f sodium perchlorate, and a mixture of 0.509 f hydrochloric and 0.039 f perchloric acids. These experiments were all conducted at 0.0° and at an ionic strength of 0.55 f. The data are presented in Table I, which also lists the value of k calculated assuming α and β are each unity. It is concluded that α and β are each unity within ±0.05 in each of the three media.

The Effect of Acid.—The effect of acid concentration was studied in mixtures of sodium perchlorate and perchloric acid, in which the ionic strength was maintained constant at 0.55 f. Data for these systems at four different temperatures are presented in Table II. It is seen that the reaction rate increases as the acidity decreases.

In this series of runs, the different oxidation states were kept separate for periods of time ranging from four hours to

TABLE II

ACID AND TEMPERATURE DEPENDENCE IN SODIUM PERCHLORATE–PERCHLORIC ACID SOLUTIONS OF IONIC STRENGTH 0.55 f

Temp., °C.	$(HClO_4)$, f	(Fe^{III}), $f \times 10^4$	(Fe^{II}), $f \times 10^4$	$t_{1/2}$, sec.	k, f^{-1} sec.$^{-1}$
0.0	0.547	...	...	...	1.35[a]
	.293	1.12	3.87	738	1.88
	.165	1.12	3.87	570	2.44
	.115	1.12	3.87	426	3.26
	.0890	1.12	3.87	372	3.73
	.0758	1.12	3.87	333	4.17
	.0508	...	...	...	6.05[a]
	.0380	1.07	3.09	241	6.91
	.0325	1.11	3.06	180	9.22
	.0200	0.760	2.72	136	14.6
	.0164	0.723	1.36	211	15.8
7.3	0.547	1.08	4.12	488	2.73
	.165	1.08	4.12	244	5.46
	.0890	1.07	2.05	250	8.87
	.0635	0.716	1.37	259	12.6
	.0509	.716	1.37	235	14.1
	.0308	.702	0.685	243	20.5
14.7	0.547	1.11	4.10	249	5.34
	.293	1.07	2.05	255	8.65
	.165	0.702	0.685	400	12.5
	.140	.702	.685	340	14.7
	.115	.702	.685	291	17.2
21.6	0.547	0.727	2.05	250	9.97
	.369	.716	1.37	239	13.9
	.293	.716	1.37	188	17.6
	.211	.760	2.72	94	21.2

[a] Mean of the appropriate order determination data listed in Table I.

TABLE III

THE RATE DEPENDENCE ON CHLORIDE CONCENTRATION IN SOLUTIONS OF IONIC STRENGTH 0.55 f

Temp., °C.	(HCl) f	$(HClO_4)$, f	(Fe^{III}), $f \times 10^4$	(Fe^{II}) $f \times 10^4$	$t_{1/2}$ sec.	k, f^{-1} sec.$^{-1}$
0.0	$< 5 \times 10^{-6}$	0.547	...	..	..	1.35[a]
	0.0254	.522	1.11	4.10	870	1.53
	.0549	.497	1.11	4.10	740	1.80
	.127	.420	1.11	4.10	550	2.42
	.254	.293	1.11	4.10	406	3.28
	.381	.166	1.11	4.10	323	4.11
	.509	.0385	...	..	..	4.81[a]
10.0	$< 5 \times 10^{-6}$	0.547	0.762	2.72	576	3.46
	0.0254	.522	.762	2.72	501	3.98
	.0509	.497	.762	2.72	443	4.50
	.127	.420	.762	2.72	318	6.26
	.254	.293	.762	2.72	236	8.44
	.254	.293	.762	2.72	236	8.44
	.381	.166	.779	2.70	180	10.9[b]
	.381	.166	.779	2.70	187	10.4
	.509	.0385	.762	2.72	163	12.2
20.0	$< 5 \times 10^{-6}$	0.547	0.762	2.72	218	9.14
	0.0254	.522	.762	2.72	185	10.8
	.0509	.497	.762	2.72	166	12.0
	.0762	.471	.762	2.72	153	13.0
	.127	.420	.762	2.72	129	15.4
	.254	.293	.762	2.72	94	21.2
	.254	.293	.762	2.72	95	21.0

[a] Mean of the appropriate order determination data presented in Table I. [b] Data obtained by measuring the growth of activity in the ferrous iron. These data are listed immediately above those obtained from the ferric fraction of the same run.

three days previous to mixing. A linear dependence (see Discussion) of R/ab upon $1/(H^+)$ was obtained despite the randomization of this additional variable. This leads to the conclusion that slow hydrolysis effects were not significant in these systems.

The Chloride Effect.—The rate dependence upon chloride ion concentration was determined in a medium whose acid concentration and ionic strength were both maintained at $0.55\,f$. Results describing this effect at three different temperatures are given in Table III. It is seen that chloride catalyzes the reaction, but not drastically.

The Effect of Inert Salts.—In the runs performed to study the effect of acid, a decrease in perchloric acid concentration was always accompanied by a corresponding increase in sodium perchlorate concentration, in order to keep both the perchlorate ion concentration and the ionic strength constant. The substitution of lanthanum perchlorate for sodium perchlorate provides a means of varying the perchlorate ion concentration while keeping the ionic strength constant or, alternatively, varying the ionic strength while keeping perchlorate ion concentration unchanged. Table IV lists the results of a series of experiments performed at approximately constant ferrous, ferric, and acid concentrations but at varying concentrations of sodium and lanthanum perchlorates. The data indicate that varying the nature and concentration of the inert salt has no significant effect on the rate constant so long as the ionic strength is unchanged. The rate constant increases with increasing ionic strength.

TABLE IV

THE RATE DEPENDENCE ON INERT SALT CONCENTRATION IN 0.0890 f PERCHLORIC ACID AT 0.0°

(Fe^{II}), $f \times 10^4$	(Fe^{III}), $f \times 10^4$	(Na^+), f	(La^{+++}), f	(ClO_4^-), f	μ, f	k, f^{-1} sec.$^{-1}$
3.87	1.12	0.456	....	0.546	0.546	3.73
4.05	1.17	0.456	....	.546	.546	3.73[a]
4.12	1.08	...	0.0751	.315	.543	3.57
4.12	1.08	0.228	....	.318	.318	3.17
4.12	1.08	...	0.1502	.541	.993	4.60

[a] The reaction mixture in this run was 7×10^{-5} in (SO_4^{--}).

Since reaction mixtures containing lanthanum perchlorate also contained trace quantities of sulfate ion, a run was therefore performed on a sodium perchlorate–perchloric acid mixture to which was added $7 \times 10^{-5}\,f$ sulfate ion. This was the concentration of sulfate ion calculated for the system containing the most lanthanum perchlorate. The results obtained for this run are also listed in Table IV. They indicate that the effect of traces of sulfate may be regarded as insignificant.

Discussion

Comparison with Previous Experiments.—If the data reported in this paper are extrapolated to the conditions of acid and temperature employed by previous workers, the rate constant thus obtained is about 10^6 times greater than the one calculated from the data of Van Alten and Rice and up to 10^7 times greater than the values derived from Kierstead's results.

It has been suggested that these wide discrepancies could be attributed to the presence of different concentrations of trace impurities. It is therefore significant that the results reported in this work are in complete agreement with earlier data obtained by a similar method[8], despite the fact that each of the materials employed in the preliminary experiments came from sources other than those which provided the materials used in these experiments. Furthermore, although every stock solution was at some time replaced by a second batch, no discontinuity in the trend of the rate data was observed. Specifically, the effect of trace concentrations of chloride and sulfate has been shown to be negligible in the present work.

Our results are in accord with those of Linnenbom and Wahl[5] and of Betts, Gilmour and Leigh[7], who observed complete exchange in the time required for the diffusion separation. Although we do not feel the present paper an appropriate place for discussion of the reasons for the discrepant results of Van Alten and Rice[4] and Kierstead,[6] it may be pointed out that their observations on the relative diffusibilities of ferrous and ferric ions are at variance with each other and with the more complete measurements of Betts, *et al.* We feel it likely that some unknown experimental difficulties may account for these discrepancies and at the same time render erroneous their inferences about the exchange rate.

The Acid Dependence.—Figures 2 and 3 show that the over-all rate constant of the reaction in perchloric acid solution is a linear function of the reciprocal of the acid concentration. The data are represented by a rate law of the form

$$\frac{R}{(Fe^{II})(Fe^{III})} = A + (B/(H^+)) \tag{4}$$

This rate law suggests that the exchange reaction proceeds through two parallel paths, one acid-independent, and the other involving species whose concentration is inversely proportional to the acid concentration. Ferric ion is appreciably hydrolyzed under our conditions, ferrous ion very much less so.[17] Hence, it is reasonable to suppose that the acid-dependent term represents the reaction between Fe^{++} and $FeOH^{++}$. We may write for the rate of the exchange

$$R = k_1(Fe^{++})(Fe^{+++}) + k_2(Fe^{++})(FeOH^{++}) \tag{5}$$

This leads to

$$\frac{R}{(Fe^{II})(Fe^{III})} = k_1\frac{(H^+)}{(H^+) + K_1} + k_2\frac{K_1}{(H^+) + K_1} \tag{6}$$

where (Fe^{II}) and (Fe^{III}) are the total concentrations of ferrous iron and ferric iron, respectively, and K_1 is the equilibrium constant for the hydrolysis reaction

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \tag{7}$$

The constant K_1 at $\mu = 0.55\,f$ may be estimated from the data of Bray and Hershey as 0.26×10^{-3} at 0° and 1.4×10^{-3} at 21.6°. Thus K_1 is never greater than about 1% of (H^+) in the acid range considered, and (6) reduces to

$$\frac{R}{(Fe^{II})(Fe^{III})} = k_1 + \frac{k_2K_1}{(H^+)} \tag{8}$$

which has the form of the observed rate law (4).

It is assumed in the above that the hydrolytic reaction is rapid. This is supported by the observations of Lamb and Jacques,[18] and by our observation that the measured exchange rate is independent of the age of the reaction solutions before mixing.

In Figs. 2 and 3, the ordinate intercept for each line yields k_1 at each particular temperature. From the slopes, values for K_1k_2 are obtained and

---

[17] (a) W. C. Bray and A. V. Hershey, *J. Am. Chem. Soc.*, **56**, 1889 (1934); (b) E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942); (c) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1332 (1950); (d) F. Lindstrand, *Svensk Kem. Tid.*, **56**, 282 (1944).

[18] A. B. Lamb and A. G. Jacques, *J. Am. Chem. Soc.*, **60**, 1215 (1938).

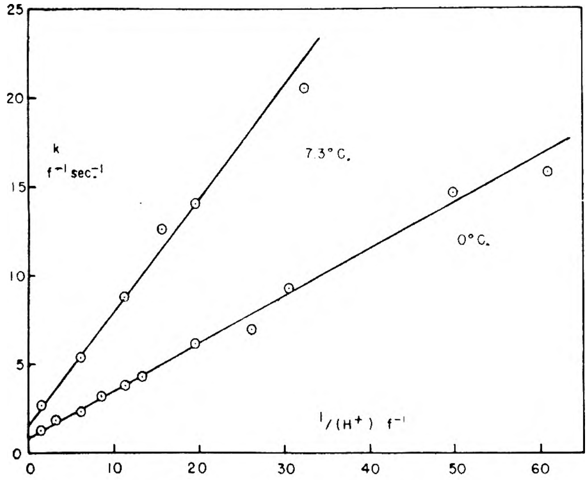


Fig. 2.—Rate *versus* reciprocal acid concentration.

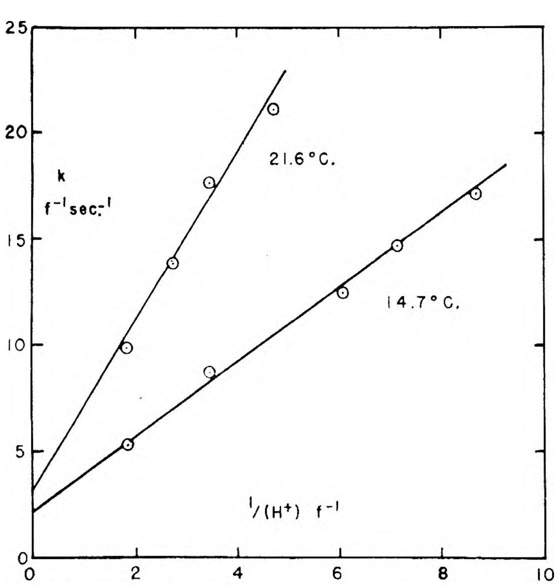


Fig. 3.—Rate *versus* reciprocal acid concentration.

by substitution of the K_1 estimates from the results of Bray and Hershey,[17a] values for k_2 can be calculated. Table V summarizes the results obtained by such an analysis.

TABLE V

RATE CONSTANTS FOR FERROUS–FERRIC EXCHANGE REACTIONS IN SODIUM PERCHLORATE–PERCHLORIC ACID

Temp., °C.	k_1, f^{-1} sec.$^{-1}$	$K_1 \times 10^3$, f	k_2, f^{-1} sec.$^{-1}$
0.0	0.87	0.256	1010
7.3	1.4	.471	1430
14.7	2.2	.850	2040
21.6	3.3	1.43	2700

Plots of log k_1 and log k_2 *versus* $1/T$ give straight lines over the temperature range 0.0 to 21.6°. The experimental activation energies found are 9.9 kcal./mole for the reaction between the unhydrolyzed ions and 7.4 kcal./mole for the acid-dependent reaction.

For simplicity of presentation, the foregoing discussion implicitly assumes that the reaction mechanism leads to products which are chemically identical with the reactants. The transfer of an uncharged (OH) radical from $FeOH^{++}$ to Fe^{++} would provide such a mechanism. If one assumed that the mechanism of the reaction involving $FeOH^{++}$ consists merely in the transfer of an electron from Fe^{++} to this species, considerations of microscopic reversibility would compel one to recognize the reverse reaction, between $FeOH^{+}$ and Fe^{+++}, as proceeding at the same rate. Under this hypothesis, the values of k_2 in Table V should be divided by 2. There seems at present no way of distinguishing between these possibilities.

The Effect of Chloride.—The data in Table III show that the rate of the reaction increases almost linearly with chloride concentration over the range 0 to 0.55 f (Cl^-). This effect, together with the fact that chloride complexes of ferric iron are known to exist under the conditions of the experiments, suggests that such complexes participate in the exchange reaction more effectively than does uncomplexed, unhydrolyzed ferric ion. Since the results of Rabinowitch and Stockmayer[17b] indicate that an appreciable fraction of the ferric iron exists as $FeCl_2^+$ as well as $FeCl^{++}$ at chloride concentrations around half formal, the approximate linearity of the rate as a function of chloride must be taken to indicate that $FeCl_2^+$ is participating in the reaction with a specific rate constant of the same order of magnitude as that for $FeCl^{++}$ but somewhat greater.

The above considerations lead to the rate expression

$$R = k_1(Fe^{++})(Fe^{+++}) + k_2(Fe^{++})(FeOH^{++}) + \\ k'(Fe^{++})(FeCl^{++}) + k''(Fe^{++})(FeCl_2^{+}) \quad (9)$$

For constant acid concentration, this leads to the expression

$$R = k(Fe^{II})(Fe^{III})\frac{1}{1 + K'(Cl^-) + K'K''(Cl^-)^2} + \\ k'(Fe^{II})(Fe^{III})\frac{K'(Cl^-)}{1 + K'(Cl^-) + K'K''(Cl^-)^2} + \\ k''(Fe^{II})(Fe^{III})\frac{K'K''(Cl^-)^2}{1 + K'(Cl^-) + K'K''(Cl^-)^2} \quad (10)$$

in which: (Fe^{II}) and (Fe^{III}) are the over-all concentrations of ferrous and ferric iron; k is the over-all second order rate constant at the given acidity in the absence of chloride; k' and k'' are the specific reaction rate constants for the reactions of $FeCl^{++}$ and $FeCl_2^+$, respectively, with ferrous ion; K' and K'' are the equilibrium constants for the reactions $Fe^{+++} + Cl^- = FeCl^{++}$ and $FeCl^{++} + Cl^- = FeCl_2^+$, respectively.

Denoting by $f(k,K',K'',Cl^-)$ the following expression, which contains only known or measured quantities

$$\frac{R\,[1 + K'(Cl^-) + K'K''(Cl^-)^2] - k(Fe^{II})(Fe^{III})}{(Fe^{II})(Fe^{III})(Cl^-)} \quad (11)$$

we obtain

$$f(k,K',K'',Cl^-) = k'K' + k''K'K''(Cl^-) \quad (12)$$

Hence a plot of $f(k,K',K'',Cl^-)$ *versus* (Cl^-) should give a straight line from whose slope and intercept k' and k'' can be calculated with the aid of the known[17b] values of K' and K''. Such graphs are given in Fig. 4.

The function (11) plotted in Fig. 4 is very sensitive to experimental errors at low chloride concentrations since it involves a small difference between measured quantities, and the scatter of the points in this region is to be expected. There seems little doubt, however, that the behavior of the function is consistent with the above assumptions.

Table VI lists the values of k' and k'' computed from this analysis, along with the values of K' and K'' used.

TABLE VI

RATE CONSTANTS FOR CHLORIDE CATALYZED FERROUS-FERRIC EXCHANGE REACTION PATHS AT IONIC STRENGTH 0.55*f*

k', specific rate constant for reaction between Fe^{++} and $FeCl^{++}$; k'', specific rate constant for reaction between Fe^{++} and $FeCl_2{}^+$

$$K' = \frac{(FeCl^{++})}{(Fe^{+++})(Cl^-)} \qquad K'' = \frac{(FeCl_2{}^+)}{(FeCl^{++})(Cl^-)}$$

Temp., °C.	K'	K''	k', f^{-1} sec.$^{-1}$	k'', f^{-1} sec.$^{-1}$
0	1.03	(0.32)	9.7	(15)
10	1.80	(0.56)	16	(32)
20	3.01	(0.94)	29	(51)

The values of the equilibrium constants used were those determined by Rabinowitch and Stockmayer,[17b] corrected to ionic strength 0.55 by the method of Bray and Hershey.[17a] It needs to be said that the temperature dependence of K'' was not measured by Rabinowitch and Stockmayer, who instead gave arguments for thinking that it should have about the same temperature coefficient as K'. In the table the numbers which are most sensitive to this assumption are placed in parentheses to indicate their doubtful character.

The energies and entropies of activation calculated for the various reaction paths are summarized in Table VII. The entropies of activation, referred to a standard state of one mole per liter of each reacting species, were calculated from the equation[19]

$$k = \frac{eKT}{h} e^{-E_{\text{exp}}/RT} e^{\Delta S^{\ddagger}/R} \qquad (13)$$

where K is the Boltzmann constant and the other symbols have their usual significance. It will be seen that the most rapid reaction path, that involving singly hydrolyzed ferric ion, has both an appreciably lower activation energy than the other paths, and a less negative entropy of activation.

TABLE VII

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE EXCHANGE REACTION OF FERROUS ION WITH VARIOUS FERRIC SPECIES

	E_{act}, kcal./mole	$\Delta S^{\ddagger}$, cal./deg.-mole
Fe^{+++} (k_1)	9.9	−25
$FeOH^{++}$ (k_2)	7.4	−18
$FeCl^{++}$ (k')	8.8	−24
$FeCl_2{}^+$ (k'')	(9.7)	(−20)

Effect of Inert Salts. The ionic strength, 0.55 *f*, employed in this work is too high to permit quantitative prediction by Debye-Hückel-Brönsted theory of the effect of ionic strength on reaction rate. It is of interest, however, to note from the data in Table IV that an increase in ionic strength leads to an increase in reaction rate, as would be expected. In view of the conclusion of Olson and Simonson[20] that the hydrolysis constant of ferric ion in perchlorate solution depends directly on the perchlorate ion concentration instead of on the ionic strength and that[21] the rate of a reaction between ions of like sign is directly influenced by the concentration of ions of opposite sign present rather than by the ionic strength, it is also of interest that the data in Table IV do not support these views. Again it must be pointed out that the data are not strictly comparable because of the high ionic strength employed in our work. Additional experiments are being carried out at low ionic strength to test this point.

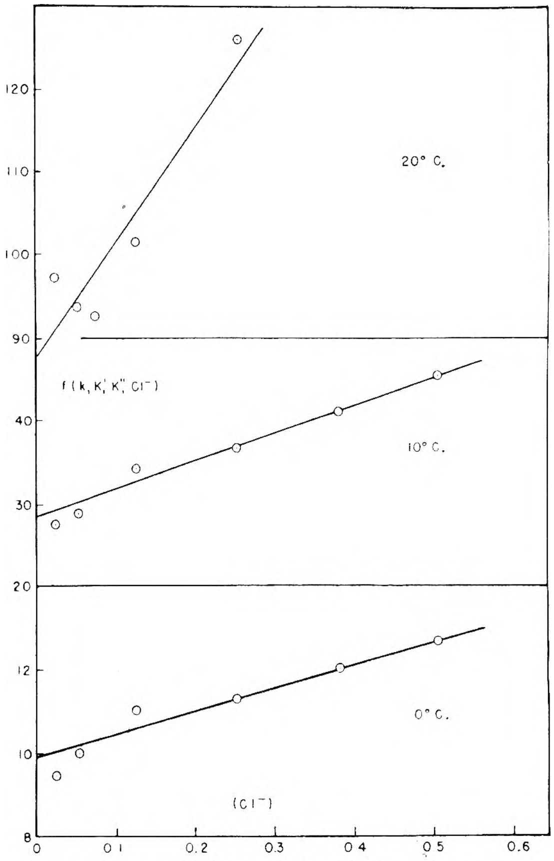


Fig. 4.—Analysis of the chloride effect.

Acknowledgment.—We wish to express our gratitude to Miss Lois Eimer for the purification of the radioactive iron, to Mr. Morris Slavin for spectroscopic analysis of the lanthanum oxide, to Mrs. Paula Campbell for her assistance in counting the samples, and to the Brookhaven National Laboratory for the funds and equipment which made this research possible.

---

[19] S. Glasstone, K. S. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

[20] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

[21] A. R. Olson and T. R. Simonson, *ibid.*, **17**, 1167 (1949).

DISCUSSION

EDWARD L. KING (University of Wisconsin).—The occurrence in the rate law of a term of the form $k(\mathrm{Fe}^{++})(\mathrm{Fe}^{+++})(\mathrm{X}^-)$ demonstrates that an activated complex of the stoichiometric composition $\mathrm{Fe}_2\mathrm{X}^{++++}$ is an important one for the exchange reaction. The two mechanisms:

I $\mathrm{Fe}^{+++} + \mathrm{X}^- \rightleftarrows \mathrm{FeX}^{++}$ a rapid equilibrium
$\mathrm{FeX}^{++} + \mathrm{Fe}^{++} \longrightarrow$ rate determining
II $\mathrm{Fe}^{++} + \mathrm{X}^- \rightleftarrows \mathrm{FeX}^{+}$ a rapid equilibrium
$\mathrm{FeX}^{+} + \mathrm{Fe}^{+++} \longrightarrow$ rate determining

are equally consistent with the term $k(\mathrm{Fe}^{++})(\mathrm{Fe}^{+++})(\mathrm{X}^-)$. Since complex ions of iron(III) are more stable than those of iron(II), the first possibility seems more reasonable. If the exchange is accomplished by an electron transfer, the activated complexes in I and II are *identical.* An X atom transfer leads to exchange only in the case of mechanism I.

ORLO E. MYERS (Oak Ridge National Laboratory).—Have you considered the possibility that perchlorate ion might be a component of the transition state in your Fe^{++}–Fe^{+++} exchange work? (Apparently $\mathrm{ClO_4}^-$ can enter into $\mathrm{I_2}$–$\mathrm{IO_3}^-$ and Hg(I)–Hg(II) cyanide exchange and perhaps the ionic strength effects observed in Tl(I)–Tl(III) exchange might be approached by considering the possibility of $\mathrm{ClO_4}^-$ participation. This might mean that all four observed paths are of the same general type.

R. W. DODSON.—This suggestion has also been made by Sutton (*Nature,* **169**, 71 (1952)). We feel that the present evidence does not permit a conclusion on this point. In the present work there is no significant evidence for a perchlorate ion effect; and the participation of perchlorate in the Hg(I)–Hg(II) exchange has the status of a speculative suggestion. We have work in progress which may give information relevant to these questions.

HERBERT C. BROWN (Purdue University).—Study of the gas phase dissociation of "bridged" molecules shows that the effectiveness of the bridging decreases from nitrogen to oxygen to chlorine. For example, in the dissociation of derivatives of trimethylaluminum [N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942)], we observed that the ease of dissociation increased in the order:

$$(\mathrm{Me_2AlNMe_2})_2 < (\mathrm{Me_2AlOCH_3})_3 < (\mathrm{Me_2AlCl})_2$$

The large difference in the rate constants observed by Silverman and Dodson for FeOH^{++} and FeCl^{++} can be understood in terms of the relative effectiveness of oxygen and chlorine in "bridging" two metal ions. In terms of the theory of electron exchange reactions proposed by Professor W. F. Libby, the smaller, better bridging atom should bring the two metal ions closer together and thereby facilitate greatly the transfer of an electron from one metal ion to the other.

If we consider that the transfer of this electron proceeds through the bridging atom or ion, it is probable that the electron affinity or polarizability of this bridging atom will be an important factor in its effectiveness in catalyzing the reaction. For example, chloride ion, in spite of its large size, might be quite effective, compared to the smaller, less polarizable fluoride ion, in serving as a better "conductor" for the transfer of the electron. In other words, the catalytic effectiveness of an ion X^- in facilitating electron transfer between two metal ions should depend upon (1) the ability of X^- to function as "bridges" and (2) the ease of transfer of the electron through the bridging ion X. We should expect the effectiveness of ions to serve as bridges to decrease in the order: $\mathrm{OH} > \mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I}$. On the other hand, their effectiveness as "conductors" should decrease in the order: $\mathrm{I} > \mathrm{Br} > \mathrm{Cl} > \mathrm{OH} > \mathrm{F}$. A study of the relative effectiveness of these ions in facilitating electron transfer should permit a quantitative analysis of the relative importance of these opposing factors.

R. W. DODSON.—Further studies of the effectiveness of anions in facilitating exchanges between different oxidation states will almost certainly give informative and interesting data, which may bear on the question of electron transfer versus atom transfer as a mechanism. We are inclined to think that the exceptionally large rate constant for FeOH^{++} may be understood in terms of a hydrogen atom transfer reaction instead of one involving only electron transfer, as discussed at the meeting. In this picture, the exchange is brought about by the transfer of a neutral hydrogen atom from the hydration sphere of ferrous ion to the OH group of the hydrolyzed ferric ion.

C. S. GARNER (U. C. L. A.).—It may be of interest to remark that King and I have submitted a letter to the Editor of *J. Am. Chem. Soc.*, describing our observations on the vanadium(II)–vanadium(III) exchange in perchloric acid, a system which formally resembles the iron(II)-iron(III) system. We found complete exchange in the dark at 2° in exchange times of the order of one minute and for concentrations of the vanadium species of *ca.* 0.06–0.1 *f*. Separation was effected with α,α'-dipyridyl in some runs, and with a cation-exchange resin in others. The possibility exists that the exchange is comparable in rate to that for the iron system. Incomplete exchange was observed between the tris-(α,α'-dipyridyl)-vanadium(II) ion and vanadium(III) ion in 0.5 *f* perchloric acid at 25° for concentrations of *ca.* 0.03 *f* for the vanadium species.

THE KINETICS OF THE EUROPIUM(II)-EUROPIUM(III) EXCHANGE REACTION[1a]

BY DALE J. MEIER[1b] AND CLIFFORD S. GARNER

The Department of Chemistry, University of California, Los Angeles 24, California

Received March 13, 1952

A kinetic study of the isotopic exchange reaction between Eu(II) and Eu(III) ions in aqueous hydrochloric acid was carried out, leading to the following rate law in the concentration range 0.026–0.068 f $EuCl_2$, 0.035–0.12 f $EuCl_3$, 0.098–1.9 f total Cl^-, 1.0 f H^+, μ adjusted to 2.0 with $NaClO_4$, 32–50°, $R = 6.5 \times 10^{11} \times \exp(-20{,}800/RT) \times [\mathrm{Eu(II)}][\mathrm{Eu(III)}][Cl^-]$ moles liter^{-1} sec.$^{-1}$. A variation in the hydrogen-ion concentration from 0.1 f to 1.6 f at constant ionic strength 2.0 is shown to affect the exchange rate by only 13%, suggesting that hydrolyzed species are of little importance in the rate-determining step, which is proposed as the exchange between hydrated Eu^{++} and a hydrated $EuCl^{++}$ ion pair. Separation of the two europium species was achieved by the use of dilute ammonium hydroxide to precipitate Eu(III) hydroxide. In chloride-free perchloric acid solutions the rate of oxidation of Eu(II) by perchlorate ions was too rapid to allow the exchange rate to be determined. The fact that the exchange rate extrapolates to zero at zero chloride-ion concentration is taken as evidence that the rate of electron transfer between the uncomplexed europium ions is a very slow reaction.

The authors[2] have previously reported that the rate of the isotopic exchange reaction between europium(II) and europium(III) in aqueous hydrochloric acid solution is measurable. Preliminary data were shown which indicated that the reaction is first order each with respect to the concentration of europium(II), europium(III) and chloride ions.

This paper describes in more detail our studies of the kinetics of this exchange reaction.

Experimental

Chemicals.—The europium, lent by Mrs. Ethel Terry McCoy, was of reported 99.9% purity. The purity was confirmed by us by determining the oxalate-oxide and oxalate-permanganate ratios.[3] Europium(III) solutions were prepared by dissolving in the appropriate acid the oxide, prepared by igniting at 850° europium(III) oxalate which had been precipitated from a hot 1 f nitric acid solution of europium(III) nitrate by the slow addition of a saturated oxalic acid solution. Europium(II) solutions were prepared by dissolving europium(II) carbonate in the appropriate acid. The carbonate was prepared by metathesizing europium(II) sulfate with hot 1 f sodium carbonate solution.[4] Europium(II) sulfate was made by reduction of europium(III) chloride solutions with a Jones reductor, followed by precipitation of the sulfate by passing the reduced solution into hot dilute sulfuric acid to which a small amount of acetic acid had been added to reduce the solubility of the precipitate.[5] The over-all yield for the conversion of europium(III) oxide to europium(II) carbonate was 90–95%.

Although europium(II) solutions are quickly oxidized by air, europium(II) carbonate resists oxidation by air if kept dry. For example, a sample of the pure carbonate which had been stored in air in a desiccator over calcium chloride for three months was found to be 96% europium(II) carbonate upon analysis by the method of McCoy.[6]

Because of the ease of oxidation of europium(II) solutions, all solutions which were to contain this ion had to be completely free of oxygen. Large quantities of each reagent solution were freed from oxygen by passing a stream of oxygen-free nitrogen through each for a period of at least 12 hours, then storing each in all-glass closed-buret systems.

The water used in this investigation was redistilled from an alkaline permanganate solution in an all-glass still. The perchloric acid was C.P. grade, redistilled at 5 mm. pressure. C.P. hydrochloric acid was redistilled to give the constant-boiling mixture. Baker C.P. fused sodium chloride, found to be iron free when tested with potassium thiocyanate, was used without further purification. C.P. sodium perchlorate was twice recrystallized from water to remove an iron impurity. The concentration of the stock sodium perchlorate solution was calculated from the solubility data of Cornec and Dickeley.[7] Oxygen-free ammonium hydroxide solutions were prepared by saturating oxygen-free water with tank ammonia. The nitrogen used in this study was scavenged of oxygen by passage through a continuously regenerated chromium(II) chloride solution.[8]

Radioeuropium Tracer.—The small amount of europium available required that it be re-used in later experiments. Thus it was desirable in preliminary experiments to use a short-lived europium activity, which would decay out after measurement and thus avoid radioactive contamination of the whole supply. Radioeuropium for the preliminary experiments was produced by Sm(p,xn) reactions in the U.C.L.A. cyclotron, using an internal beam of *ca.* 16-Mev. protons. Chemical separation of europium from the samarium oxide targets by the procedure of Meinke[9] gave europium activities of the following half-lives: 53 days, 4.8 days, 20 hours and 8 hours. The latter two activities predominated greatly for the bombardment times used. At the time of this investigation only the 4.8-day activity had not been reported. Later Hoff, Rasmussen and Thompson[10] reported this activity among those they observed after proton bombardment of samarium.

After completion of the preliminary experiments it was desirable to use a longer-lived activity to avoid frequent processing of cyclotron targets and the large decay corrections necessary with the short-lived activities. Through the coöperation of Professor Don M. Yost and Dr. David L. Douglas of the California Institute of Technology we obtained a sample of 5.2-year Eu^{152} prepared a year earlier by irradiation of spectroscopically pure europium oxide in the Oak Ridge pile. Radiochemical experiments made by us on the aged sample showed that europium was the only radioactive element present. The stock solution of Eu^{152} (*ca.* 1 mc.) consisted of 1.5 mg. of europium(III) chloride in 5 ml. of dilute hydrochloric acid. For each exchange experiment *ca.* 20 µl. of this stock solution was sufficient to give a satisfactory counting rate, thus requiring no correction for the volume of solution or europium added in introducing the activity.

Measurement of Radioactivity.—Other than in a few preliminary experiments in which mounted precipitates were counted, all radioassays were made on solutions, using dipping counters with a scale-of-64 circuit. The solutions were diluted to a definite volume, usually 20 ml., in a 30-ml. test-tube, and the dipping Geiger tube was accurately adjusted with respect to the test-tube with a rack and pinion

---

[1] (a) Abstracted from the Ph.D. thesis of Dale J. Meier, University of California, Los Angeles, June, 1951; (b) University Fellow, 1949–1951. Present address: Shell Development Company, Emeryville, California.

[2] D. J. Meier and C. S. Garner, *J. Am. Chem. Soc.*, **73**, 1894 (1951).

[3] D. W. Pearce, G. L. Barthauer and R. G. Russell, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 58.

[4] R. A. Cooley and D. M. Yost, *ibid.*, p. 71.

[5] J. K. Marsh, *J. Chem. Soc.*, 398, 525 (1942).

[6] H. N. McCoy, *J. Am. Chem. Soc.*, **61**, 2455 (1939).

[7] E. Cornec and J. Dickeley, *Bull. soc. chim. France*, **41**, 1017 (1927).

[8] H. W. Stone, *J. Am. Chem. Soc.*, **58**, 2591 (1936).

[9] W. W. Meinke, AECD-2738 (1949).

[10] R. W. Hoff, J. O. Rasmussen and S. G. Thompson, *Phys. Rev.*, **83**, 1068 (1951).

assembly so as to give reproducible geometry. Since the solutions to be counted were of constant chemical composition, absorption and scattering corrections were unnecessary. Background (*ca.* 12 c./min.) and small coincidence corrections were applied. Each sample was counted for a time sufficient to reduce statistical counting errors to less than 1% standard deviation.

Separation Methods.—Unsuccessful methods tried for the separation of europium(II) from europium(III) included the use of sulfate ion to precipitate europium(II) sulfate, and the use of buffered phosphate, oxalate and formate solutions to precipitate one or the other of the reactants. Separation of the two reactants with sulfate ion gave unreproducible (and often very large) zero-time exchange traced to coprecipitation of europium(III) by the europium(II) sulfate. The sulfate method was used in preliminary experiments to show that the exchange was slow. Dilute ammonium hydroxide, which precipitates europium(III) hydroxide, was found to give a quantitative separation of the two ions, and gave reproducible amounts of zero-time exchange.

Procedure.—Portions of europium(III) oxide and europium(II) carbonate were weighed into separate 50-ml. glass-stoppered erlenmeyer flasks fitted with nitrogen inlet and outlet tubes. After the flasks were flushed with nitrogen, calculated quantities of reagents were added from the reagent storage systems to each flask to give a volume of 6.00 ml. Tracer europium(III) chloride (*ca.* 20 μl.) was added to the flask containing the europium(III). The resulting europium(II) and europium(III) solutions were separately equilibrated at the desired temperature in an oil-bath. Nitrogen was passed through the europium(II) solution to remove the carbon dioxide resulting from the reaction of the carbonate with the acid, since the presence of carbon dioxide would have interfered with the separation method. After temperature equilibrium was reached 5.00 ml. of each solution was transferred with an automatic pipet to the reaction vessel and mixed quickly by bubbling nitrogen through the solution. The reaction vessel was similar to one described by Lewis.[11] It consisted of a 20-ml. spherical reaction chamber fitted with a pipet from which aliquots could be withdrawn without opening the vessel to the air. Nitrogen could be passed through the system. Surrounding the reaction chamber was an opaque jacket through which oil from a thermostated oil-bath was pumped to maintain a temperature constant to ±0.1°.

The concentration of europium(II) in the exchange solution was determined during each exchange run by the method of McCoy.[6] A known volume of the exchange solution, withdrawn at *ca.* the half-time of the reaction, was delivered into 10 ml. of oxygen-free 0.1 *f* iron(III) ammonium sulfate solution. After the addition of a few drops of 85% phosphoric acid to reduce the color of the iron(III) ions, the iron(II) resulting from the reduction of iron(III) by the divalent europium was titrated with a standard potassium permanganate solution. The europium(II) concentration was usually *ca.* 95% of that calculated from the amount of europium(II) carbonate used to prepare the exchange solution, the difference resulting from partial oxidation of divalent europium by air during the transfer to the reaction vessel. The concentration of europium(III) was taken as the difference between the total europium concentration and the europium(II) concentration.

At desired times 2-ml. aliquots were withdrawn from the reaction vessel and delivered in a current of nitrogen into 10 ml. of 1.5 *f* ammonium hydroxide solution in a 50-ml. centrifuge tube equipped with a ground-glass stopper. After the centrifuge tube was capped the mixture was shaken gently and centrifuged. Tests showed that europium(III) was quantitatively precipitated under these conditions, with little or no coprecipitation of europium(II). The supernatant solution was poured off, and a few drops of 6% hydrogen peroxide was added to it to oxidize the divalent europium. The precipitate which formed was centrifuged, washed with water, then dissolved in 2 ml. of 6 *f* hydrochloric acid and diluted to volume in the test-tube used for the radioassay with the dipping counter.

The europium content of each radioassayed fraction was determined as follows by the method of Meinke.[9] Europium was precipitated by addition of an excess of ammonium hydroxide, the precipitate centrifuged, washed, and then dissolved in 10 ml. of 0.6 *f* hydrochloric acid. This solution was heated to boiling and 10 ml. of a saturated oxalic acid solution was added. After cooling on an ice-bath for 10 minutes the precipitate of europium(III) oxalate decahydrate was filtered onto a tared fritted-glass crucible. The precipitate was washed in turn with 10 ml. each of water, absolute ethanol, and diethyl ether, then dried in a vacuum desiccator for 10 minutes, and weighed as the decahydrate.

With the above experimental conditions it was necessary to follow the exchange by measurement of the change in specific activity of the europium(II) fraction. A change of specific activity of the europium(III) fraction can arise from three sources: the exchange reaction, partial oxidation of europium(II) to europium(III) during their separation, and partial coprecipitation of europium(II) in the europium(III) hydroxide precipitate. The exchange reaction is the only factor causing a change in the europium(II) specific activity.

Results

Exchange in the Absence of Chloride Ion.—Originally we planned to study the exchange reaction in aqueous perchloric acid solution to avoid effects arising from complex-ion formation. However, this plan had to be modified when it was found that europium(II) was completely oxidized in perchlorate solution before the exchange had proceeded more than a few per cent. The oxidation was faster than the exchange under all conditions tried, namely, 0.1–2 *f* perchloric acid, 25–50°, absence of light. As shown below, the exchange is catalyzed by chloride ion, and it proved possible to study the exchange as a function of the chloride-ion concentration by substituting perchlorate for chloride ion. The rate of oxidation of europium(II) by perchlorate, relative to the exchange rate, was slow at chloride-ion concentrations above 0.1 *f*. By studying the rate as a function of the chloride-ion concentration it was hoped that the data could be extrapolated to zero chloride-ion concentration, and in this manner the exchange rate for the non-complexing solutions determined. However, the extrapolated rate was essentially zero relative to the rate at 0.1 *f* chloride ion.

Apparent Zero-Time Exchange.—The exponential exchange law[12,13,14] applied to the europium(II)–europium(III) exchange, takes the form

$$Rt = -\frac{[\mathrm{Eu(II)}][\mathrm{Eu(III)}]}{[\mathrm{Eu(II)}] + [\mathrm{Eu(III)}]} \ln (1 - F) \qquad (1)$$

where R represents the rate at which europium(II) becomes europium(III), and *vice versa;* this rate is independent of the presence of tracer levels of radioeuropium, and is a constant when all conditions other than the isotopic distribution are held constant. F is the fraction exchange at time t, and is given by

$$F = \frac{S_{(\mathrm{II})} - S_{(\mathrm{II})0}}{S_\infty - S_{(\mathrm{II})0}} \qquad (2)$$

where $S_{(\mathrm{II})}$ and $S_{(\mathrm{II})0}$ are the specific activities of europium(II) at time t and time zero, respectively, and S_∞ is the equilibrium specific activity. In this investigation specific activities were arbitrarily expressed in counts per minute per milligram of europium(III) oxalate decahydrate. The equilibrium specific activity was usually determined as the average specific activity of all the europium in the exchange mixture, although it was experimentally determined for europium(II) in a few exchange runs as a check. Concentrations (bracketed quantities) are expressed in terms of gram atoms of europium per liter of solution at 25°.

The expected exponential exchange behavior was exhibited in all runs. There was a reproducible zero-time exchange, which increased from *ca.* 7 to 20% as the hydrogen-ion concentration of the exchange solution was decreased from 1.6 to 0.1 *f* at an ionic strength of 2.0. The work of Prestwood and Wahl[15] showed that when separation-in-

---

[11] W. B. Lewis, Technical Report No. 19, Laboratory for Nuclear Science and Engineering, Mass. Inst. of Tech., 1949.

[12] H. A. C. McKay, *Nature*, **142**, 997 (1938).

[13] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 287.

[14] A. C. Wahl and N. A. Bonner (editors), "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1 by O. E. Myers and R. J. Prestwood.

[15] R. J. Prestwood and A. C. Wahl, *J. Am. Chem. Soc.*, **71**, 3137 (1949). Also see Appendix I of reference 14.

duced exchange and the degree of separation are constant the slope of ln $(1 - F)$ *versus* t is unchanged and the data may be corrected for such effects.

Dependence of Exchange Rate on Europium(II) and Europium(III) Concentrations.—If the exchange rate is first order each in europium(II) and europium(III)

$$R = k_1[\mathrm{Eu(II)}][\mathrm{Eu(III)}] \qquad (3)$$

where k_1 is a specific rate constant when all possible rate-determining species other than europium are maintained at constant concentration. The exchange half-time, $t_{1/2}$, is then inversely proportional to the total europium concentration

$$t_{1/2} = \frac{0.693}{[\mathrm{Eu(II)}] + [\mathrm{Eu(III)}]} \times \frac{1}{k_1} \qquad (4)$$

TABLE I

ORDER WITH RESPECT TO EUROPIUM(II) AND EUROPIUM(III)

$[H^+] = 1.00 f$, 39.4°, $\mu = 2.0$

Total Eu concn., f	Eu(II) concn., f	Eu(III) concn., f	Cl^- concn., f	Half-time, minutes
0.0603	0.0258	0.0345	1.88	59
.0653	.0244	.0409	1.86	53
.0894	.0258	.0636	1.82	40
.1055	.0683	.0372	1.84	33
.1465	.0270	.1195	1.51	29

Table I presents the data concerning this dependence. The chloride-ion concentration varied slightly, for which effect a correction may be applied by anticipating later data which show the exchange rate to be dependent on the first power of the chloride-ion concentration and to occur through only one exchange path. Equation 4 may then be generalized to

$$t_{1/2} = \frac{0.693}{\{[\mathrm{Eu(II)}] + [\mathrm{Eu(III)}]\}[\mathrm{Cl}^-]} \times \frac{1}{k} \qquad (5)$$

Figure 1 shows data plotted as suggested by equation 5. The intercept is zero within the experimental error, and the first-order dependence for europium(II) and for europium(III) assumed in deriving equations 4 and 5 is indicated.

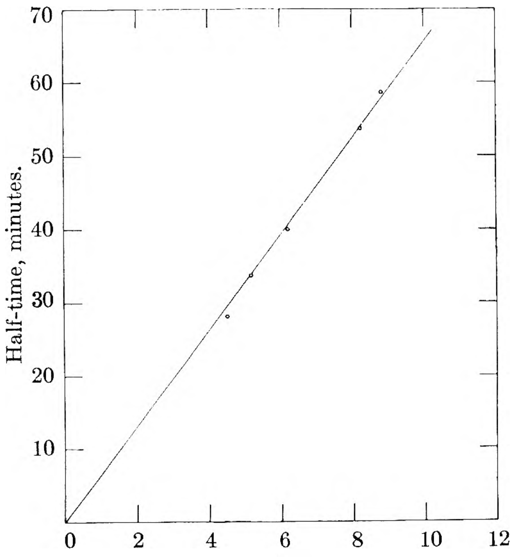


Fig. 1.—Effect of total europium (and chloride) concentration on the half-time ($[H^+] = 1.00 f$, $[Cl^-] = 1.5$–$1.9 f$, 39.4°, $\mu = 2.0$).

The usual method of determining dependence of the reaction rate on the concentration of a reactant, *i.e.*, by evaluating $\partial \log R/\partial \log [\mathrm{Eu(II)}]$ and of $\partial \log R/\partial \log [\mathrm{Eu(III)}]$, with the other concentrations held constant, was also carried out as a confirmatory check of equation 5. The values found were 1.02 and 1.03 for the order of the reaction with respect to europium(II) and europium(III), respectively, an excellent confirmation of first-order dependence for each species.

Dependence of Exchange Rate on Chloride-Ion Concentration.—The greatly enhanced rate resulting when chloride was substituted for perchlorate suggests that chloride-associated species were important in determining the exchange rate. Representative data obtained when the chloride-ion concentration was varied over wide limits are presented in Table II. If we assume that both the uncomplexed and chloride-complexed europium species can exchange, then R is given as

TABLE II

ORDER WITH RESPECT TO CHLORIDE ION

$[H^+] = 1.00 f$, 39.4°, $\mu = 2.0$

Cl^- concn., f	Total Eu concn., f	Half-time, minutes
0.0982	0.0600	870
0.716	.0677	132
1.51	.1465	29
1.86	.0653	53

$$R = [\mathrm{Eu(II)}][\mathrm{Eu(III)}]\{k_1 + k[\mathrm{Cl}^-]^n\} \qquad (6)$$

and the half-time is related to chloride-ion concentration by the equation

$$\frac{0.693}{[\mathrm{Eu(II)}] + [\mathrm{Eu(III)}]} \times \frac{1}{t_{1/2}} = k_1 + k[\mathrm{Cl}^-]^n \qquad (7)$$

If the left side of equation 7 is plotted against the chloride-ion concentration raised to the appropriate power n, a straight line will be obtained of slope k and intercept k_1. Figure 2 gives a plot with $n = 1$. A straight line is obtained over a 19-fold change in chloride-ion concentration, and with a zero intercept within experimental error.

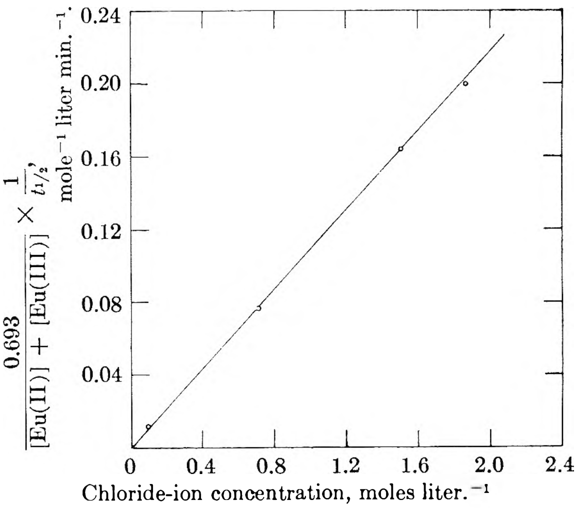


Fig. 2.—Effect of chloride-ion concentration on the exchange rate ($[H^+] = 1.00 f$, 39.4°, $\mu = 2.0$).

Dependence of Exchange Rate on Hydrogen-Ion Concentration.—Table III summarizes the data obtained when the hydrogen-ion concentration was varied with the total europium and chloride-ion concentrations held roughly constant. If the exchange rate is independent of hydrogen-ion concentration over the range of interest, equation 7 is applicable, with $k_1 = 0$ and $n = 1$ as experimentally demonstrated, giving

$$k = \frac{0.693}{\{[\mathrm{Eu(II)}] + [\mathrm{Eu(III)}]\}[\mathrm{Cl}^-]} \times \frac{1}{t_{1/2}} \qquad (8)$$

The rate constant k, calculated from equation 8 and given in the last column of Table III, increases systematically by *ca.* 13% over the 16-fold increase in hydrogen-ion concentration. This trend is opposite to the hydrolysis effect observed by Prestwood and Wahl[15] and by Harbottle and Dodson[16] for the thallium(I)-thallium(III) exchange. It seems

---

[16] G. Harbottle and R. W. Dodson, *J. Am. Chem. Soc.*, **73**, 2442 (1951).

reasonable to believe that a primary result of hydrolysis might be to lower the coulombic barrier separating the reacting ions, thus allowing closer average approach with a concomitant increase in the exchange rate. These considerations, coupled with the small effect observed and the known strongly basic properties of europium(III) and europium(II), suggest that hydrolysis does not play an important part in the exchange at the concentrations used in this investigation. We believe that the variation in rate can best be explained by specific electrolyte activity effects resulting when sodium ion is substituted for hydrogen ion in maintaining constant ionic strength.

Table III

Order with Respect to Hydrogen Ion

39.4°, $\mu = 2.0$

H^+ concn., f	Total Eu concn., f	Cl^- concn., f	Half-time, minutes	1000 k, moles^{-2} liter^2 sec.$^{-1}$
0.10	0.0596	1.89	64	1.60
0.30	.0630	1.97	58	1.68
1.00				1.80[a]
1.56	.0615	1.72	60	1.82

[a] Average of data from Table I.

Activation Energy.—Figure 3 summarizes the results obtained by varying the reaction temperature. The experimental molar activation energy determined from the slope is 20.8 ± 0.9 kcal. The rate constant may be represented as

$$k = 6.5 \times 10^{11} e^{-20{,}800/RT} \text{moles}^{-2}\text{liter}^2\text{sec.}^{-1} \quad (9)$$

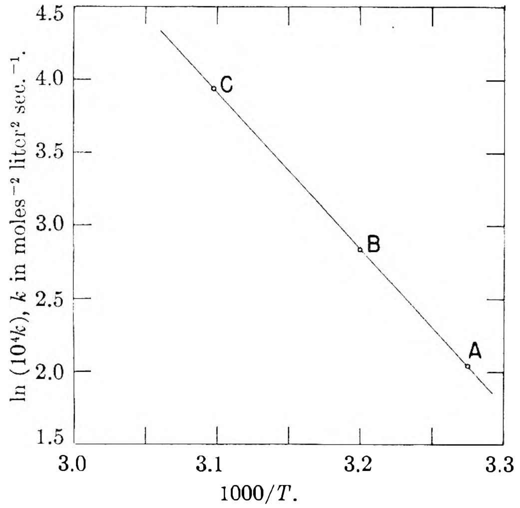


Fig. 3.—Temperature dependence of exchange rate ($[H^+] = 1.00 f$, $\mu = 2.0$); A, 31.7°, 0.0634 f total Eu, 1.88 f Cl^-, 124 min. half-time; B, 39.4°, average of data from Table I; C, 49.5°, 0.0523 f total Eu, 1.89 f Cl^-, 22 min. half-time.

Catalysis by Light.—In one of the later experiments the opaque covering of the reaction vessel was removed and light from a 300-watt incandescent lamp was focused on the vessel. A slight increase in the specific rate constant was noted, and traced to an observed increase in temperature (*ca.* 1°) of the solution.

Heterogeneous Catalysis.—In one series of experiments glass wool was placed in the solution. The glass wool, which was carefully cleaned with boiling nitric acid before use, was calculated to have increased the surface exposed to the solution by a factor of five. The specific rate constant in the presence of glass wool was found to agree with that observed in the absence of the glass wool to within 1%. An attempt was made to determine the effect of a piece of platinized platinum wire on the exchange rate. Hydrogen was rapidly liberated at the wire surface in contact with the exchange solution. A few minutes later europium(II) could not be detected in the solution.

Discussion

The first-order dependence of the exchange rate on chloride-ion concentration indicates that the activated state includes a monochloro-complexed europium species. From the kinetic studies it is not possible to conclude which of the two ions forms the complex, but it seems most reasonable to assume that it is europium(III). Halo-complexes of trivalent rare earths have been reported by Connick and Mayer[17]; for the monochloro-complex of cerium(III) they report an association constant of *ca.* 2 (that for europium(III) would be expected to be nearly the same). It seems unlikely that the association constant is this high, for the spectroscopic work of Freed[18] and the polarographic work of Holleck[19] have indicated no detectible complex-ion formation between europium(III) and chloride. Moreover, the absorption spectra of aqueous solutions of eleven rare-earth(III) perchlorates and chlorides, including europium and cerium, are essentially identical.[20] In the present study, the exchange rate is proportional to the chloride-ion concentration over the 19-fold range of concentration investigated (see Fig. 2); saturation effects which should be observable if the association constant were as great as 2 are not apparent.

The apparent zero intercept of Fig. 2 shows that the rate of electron transfer between the uncomplexed ions is very slow compared to the rate of the chloride-catalyzed reaction.

The exchange mechanism can be formulated in at least two ways: (1) A small fraction of one of the reactants, probably Eu(III), is complexed with chloride ion, and in the rate-determining step one electron is transferred between the chloro-complexed species and the other reactant

$$Eu^{*+++} + Cl^- \rightleftharpoons Eu^*Cl^{++} \qquad \text{(rapid equilibrium)}$$

$$Eu^*Cl^{++} + Eu^{++} \longrightarrow Eu^*Cl^+ + Eu^{+++} \qquad \text{(rate determining)}$$

$$Eu^*Cl^+ \longrightarrow Eu^{*++} + Cl^- \qquad \text{(rapid follow reaction)}$$

(2) This reaction mechanism is identical to that of 1 except that an electron and a chloride ion are interchanged between reactants in the activated complex, either simultaneously or in two steps

$$Eu^{*+++} + Cl^- \rightleftharpoons Eu^*Cl^{++} \qquad \text{(rapid equilibrium)}$$

$$Eu^*Cl^{++} + Eu^{++} \longrightarrow Eu^{*++} + EuCl^{++} \qquad \text{(rate determining)}$$

Comparison of the true energy and entropy of activation for this reaction with that predicted from absolute rate theory for reactions between ions of this charge type is not possible at present as the experimental rate constants and activation energy include the unknown association constant and heat of formation of the chloro-complexed ion.

Acknowledgment.—The authors wish to express their sincere appreciation to Mrs. Ethel Terry McCoy for the loan of the europium used in this investigation, and to Professor Don M. Yost and Dr. David L. Douglas for the Eu^{152} activity.

---

(17) R. E. Connick and S. W. Mayer, *J. Am. Chem. Soc.*, **73**, 1176 (1951).

(18) S. Freed, *Rev. Mod. Phys.*, **14**, 105 (1942).

(19) L. Holleck, *Z. Elektrochem.*, **46**, 59 (1940).

(20) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

DISCUSSION

N. Uri (Chicago).—I would like to ask the authors how much is known on ion pair complex formation between Eu^{3+} and Cl^-? If complex formation is very weak I think it should be attributed to an accidentally large endothermicity. It appears that in practically all cases ion pair complex formation in aqueous solution is accompanied by a considerable positive entropy change which goes hand in hand with the positive entropy changes accompanying the desolvation of the negative ion. On the other hand, the heat changes result, as can be demonstrated by a thermodynamic cycle, from differences between very large values. The free energy change of ion pair complex formation is thus composed of a regular positive entropy change and an accidental heat change. If the latter happens to be very endothermic, ion pair complex formation would not be observed, at least at room temperature.

C. S. Garner.—Complex formation between Eu^{3+} and Cl^- is discussed in the paper. Apparently no direct evidence exists for chloro-complexed species of Eu^{3+}. Spectroscopic and polarographic studies indicate no detectable complex-ion formation in this system, and no thermodynamic data are available for any halo-complexes of europium(III).

S. E. Voltz (Houdry Process Corp.).—You have demonstrated that increasing the amount of glass surface does not affect the reaction rate, which indicates that glass does not catalyze this reaction. This result is listed under "Heterogeneous Catalysis" and I would like to know, if you consider this particular result as indicative of the possible behavior of other heterogeneous catalysts. Would you also comment on the effect observed in the presence of platinized platinum wire?

Garner.—The experiments performed with an increased glass surface were undertaken solely to find out if the glass container and transfer pipets were having an appreciable effect on the rate of the exchange reaction; no such effect was found. Inasmuch as there are certain features common to electron-transfer exchange and electrode reactions, one may assume that there may well be certain substances that act as heterogeneous catalysts for the exchange just as there exist such catalysts for electrode reactions.

The rapid liberation of hydrogen at the surface of a platinized platinum wire in contact with the exchange solution, and the consequent rapid disappearance of europium(II) from the solution presumably imply that the platinum catalyzes the oxidation of europium(II) by water (or hydrogen ion). Inasmuch as the formal reduction potential of the Eu(II)-Eu(III) couple is approximately +0.43 volt at 25°, there is a large thermodynamic driving force for the oxidation of europium(II) by water. In such an oxidation there is a transfer of an electron from each europium(II) ion, and apparently the metallic platinum provides an easy path for this electron transfer.

Orlo E. Myers (Oak Ridge Nat. Lab.).—Would you care to amplify your discussion of the observed high activation energy for Eu(II)-Eu(III) exchange? It is about twice that for other one-electron transfer systems we know and of the order of that generally observed for two-electron transfer.

Garner.—The observed activation energy for the europium(II)-europium(III) exchange does appear to be somewhat large relative to the few values which have been obtained so far for one-electron-transfer systems. However, the apparent activation energy includes an unknown contribution from the heat of formation of the chloro-complexed ion (or ion pair); the true activation energy would presumably be appreciably smaller after correction for this factor. *E.g.*, a correction of 7 kcal./mole would bring the activation energy down to that found for the one-electron exchange between the tris-(ethylenediamine) complexes of cobalt(II) and cobalt(III).

ELECTRON TRANSFER PROCESSES AND THE OXIDATION-REDUCTION REACTIONS OF HEXACYANOFERRATE(III) ION IN AQUEOUS SOLUTION[1]

By Arthur W. Adamson

The Chemical Laboratories of the University of Southern California, Los Angeles, California

Received March 13, 1952

The oxidation-reduction reactions of hexacyanoferrate(III) ion are shown to be rapid whenever the process involves a simple electron transfer, and to be slow and of complex mechanism if such a step cannot occur. Reactions of the first type, one electron transfer exchange processes in general, are shown to follow a correlation based on the magnetism (or net angular momentum) of the ions. The kinetics of one of the reactions of the second type, the oxidation of cyanide ion, was studied, and is shown to lead to definite conclusions about the type of mechanism involved.

The reactions of hexacyanoferrate(III) ion as an oxidizing agent seem to fall into one or the other of two classes. The first comprises those reactions that appear to involve no more than a simple electron transfer. The reactions in this class have, so far, the common characteristic of being very rapid. The immeasurably fast exchange between hexacyanoferrate(II) and hexacyanoferrate(III) ions[2,3,4a] constitutes the simplest example, but others include the instantaneous oxidation of the cobalt(II) pentacyanide complex to pentacyanoaquocobaltate(III) ion,[4b] and the rapid oxidation of hexacyanomanganate(II) ion to the corresponding manganese(III) complex.[5] The color change accompanying this last reaction occurs in less than 10^{-2} second, as judged by the use of a flow mixing apparatus of the type referred to by Awtrey and Connick.[6] The speed of these reactions between highly charged ions raises doubts about the importance of coulomb repulsion as the main deterrant to electron exchange. Lewis, *et al.*,[3] reached a similar conclusion from a consideration of their measured activation energies for the exchange between tris-ethylenediaminecobaltate(II) and the corresponding cobalt(III) complex.

These doubts have led to a consideration of other factors. Weiss[7] has suggested that dissolved oxygen acts as a variable factor to make some exchange processes faster than would be expected, although Dodson, *et al.*,[8] report that there is no effect of deaeration on the Fe(II)-Fe(III) exchange, and the diffusional separation of hexacyanoferrate(II)-hexacyanoferrate(III) mixtures[4a] was also carried out with deaerated solutions.

A rather different correlating factor is here suggested. The various electron exchange systems that have been studied are collected in Table I, together with values for the magnetic moments. Examination of the table makes it evident that the electron exchange tends to be slow for a pair of ions of high magnetic moment, particularly if there is a large difference in the two values. Actually, the product of the sum and difference in moments indexes the pairs in the approximate

Table I

Electron exchange pair		Magnetic moments[a] (Bohr magn.)		Sum × Diff.	Order of half-life for exchange
Eu(II)	Eu(III)	8	3.5	52	100 hr.[10]
$Co(en)_3^{++}$	$Co(en)_3^{++}$	4.9	0	24	10 hr.[3]
$Co(NH_3)_6^{++}$	$Co(NH_3)_6^{++}$	4.9	0	24	90 d.[3]
Co^{++}	Co^{+++}	4.9	0	24	1 min.[16a,b]
Mn(II)	Mn(III)	5.9	5.0	10	Less than 1 min.[11]
Ce(III)	Ce(IV)	2.5	0	6	10 min.[12]
$Mn(CN)_6^{-4}$	$Mn(CN)_6^{-3}$	2.3	*ca.* 3.3	6	Short, but probably measurable[5]
Fe(II)	Fe(III)	5.2	5.7	6	20 sec.[13, 9]
$Os(bip)_3^{++}$	$Os(bip)_3^{+++}$[b]	(0)	(1.7)	3[c]	1 min.[14]
$Fe(CN)_6^{-4}$	$Fe(CN)_6^{-3}$	0	1.7	3	Fast[2,3,4a]
$MnO_4^{=}$	MnO_4^{-}	1.7	0	3	Fast[11, 15]
Hg(I)	Hg(II)	(1.7 if Hg^+)	0	3	Fast[16]
Co(II)P	Co(III)P[d]	1.7	0	3	Fast[9]

[a] Susceptibilities, if not in the article(s) referred to, are taken from P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943. [b] Tris-(2,2′-bipyridyl). [c] The susceptibilities are probably larger, since quenching of the orbital moments tends to be incomplete for second and third row transition elements. [d] Tetraphenylporphine.

---

[1] Investigations carried out under contract N6onr-23809 between the Univ. of Southern California and the Office of Naval Research.

(2) R. C. Thompson, *J. Am. Chem. Soc.*, **70**, 1045 (1948).

(3) W. B. Lewis, C. D. Coryell and J. W. Irvine, Jr., *J. Chem. Soc.*, *Supplement No. 2*, 5386 (1949).

(4) (a) J. W. Cobble and A. W. Adamson, *J. Am. Chem. Soc.*, **72**, 2276 (1950); (b) A. W. Adamson, *ibid.* **73**, 5710 (1951).

(5) Unpublished work in this Laboratory.

(6) A. Awtrey and R. Connick, *J. Am. Chem. Soc.*, **73**, 1341 (1951).

(7) J. Weiss, *J. Chem. Phys.*, **19**, 1066 (1951).

(8) R. W. Dodson, L. Eimer and A. Medalia, Quarterly Progress Report, Brookhaven National Laboratory, July-September, 1951.

(9) G. D. Dorough and R. W. Dodson, Quarterly Progress Report, Brookhaven National Laboratory, July-September, 1951.

(10) D. J. Meier and C. S. Garner, This Journal, **56**, 853 (1952).

(11) A. W. Adamson, *ibid.*, **55**, 293 (1951).

(12) J. Gryder and R. Dodson, *J. Am. Chem. Soc.*, **71**, 1894 (1949).

(13) R. W. Dodson, *ibid.*, **72**, 3315 (1950).

(14) F. P. Dwyer and E. C. Gyarfas, *Nature*, **166**, 481 (1950).

(15) H. C. Hornig, G. L. Zimmerman and W. F. Libby, *J. Am. Chem. Soc.*, **72**, 3808 (1950).

(16) E. L. King, *ibid.*, **71**, 3553 (1949).

(16a) S. Hoshowsky, O. Holmes and K. McCallum, *Can. J. Research*, **27B**, 258 (1949).

(16b) H. L. Friedman, J. P. Hunt, R. A. Plane and H. Taube, *J. Am. Chem. Soc.*, **73**, 4028 (1951); the authors suggest that the lability of the Co(III)·Aq ion may be due to the presence of an equilibrium trace of the paramagnetic ionic form of the aquated ion.

order of exchange half-lives. As was noted by Dorough and Dodson,[9] exchange between the amine type complexes of cobalt may well be exceptionally slow because of the change from ionic to covalent bonding that occurs.

This correlation, as such, has predictive value. Thus, the very recent report of a fast exchange between a cobalt(II) and cobalt(III) porphine complex[9] could have been predicted on the grounds that the cobalt(III) complex was diamagnetic, and the cobalt(II) complex had a moment corresponding to only one unpaired electron.

Another type of prediction would be that the net reaction between two oxidation–reduction couples could be slow even though a simple electron transfer was involved, and the electron exchange was fast for each pair separately. This case would arise if, for each couple, the change in magnetism is small, but at very different levels. A specific example is the reaction

$$\mathrm{Hg(II)} + \mathrm{Fe(II)} = \mathrm{Hg(I)} + \mathrm{Fe(III)} \qquad (1)$$

For the uncomplexed ions (but Hg(I) taken as Hg_2^{++}), the standard potential for (1) is 0.14 volt.[17] The electron exchanges between Hg(II) and Hg(I), and between Fe(II) and Fe(III) are rapid, but the above reaction should be slow in view of the diamagnetism of Hg(II) and the high paramagnetism of Fe(II). The fact that Hg(I) exists primarily as a dimer should not present any more of an obstacle to this reaction than it does to the electron exchange with Hg(II), especially since the rather large dissociation constant for Hg_2^{++} reported by Higginson[18] makes it probable that the monomer is the intermediate.

In view of this prediction, the rate of (1) is being studied, and preliminary results indicate it to be quite small. The reaction mixture consisted of 10^{-3} *M* mercuric nitrate and ferrous nitrate, in 1 *M* perchloric acid. The half-life is of the order of several days, as followed spectrophotometrically at 270 mu, at which wave length, the only species having a large extinction coefficient is Fe(III).[19] As a check on the position of the equilibrium point, no reaction occurred when Hg(I) and Fe(III) were the starting species. The reaction is catalyzed by an iron surface.

The explanation of this correlation is so far obscure. It seems unlikely that the magnetic moments, *per se*, are involved, in view of the low degree of interaction between magnetic and electric fields. It may be that it is the unquenched orbital and spin angular moments, as reflected by the susceptibilities, that are significant. Selection rules of the type restricting the angular momentum change for atomic and molecular electronic transitions may operate for the electron transfer process. If so, however, this would be in spite of the Stark effect which tends to make possible for ions in solution transitions which normally are forbidden.[19]

The second group of reactions of hexacyanoferrate(III) ion includes the oxidation of iodide, of thiosulfate (to tetrathionate ion), of sulfite, and of cyanide ions. These reactions are relatively slow, and their kinetics complicated. Thus, the reaction

$$2Fe(CN)_6^{-3} + 2I^- = 2Fe(CN)_6^{-4} + I_2 \qquad (2)$$

has been studied by a number of people,[20] with some variability in results. The rate is approximately first order in hexacyanoferrate(III), and first to second order in iodide; it is faster in acid solution, and is retarded by hexacyanoferrate(II). Wagner[20] proposed the mechanism

$$Fe(CN)_6^{-3} + 2I^- \rightleftarrows Fe(CN)_6^{-4} + I_2^- \qquad (3)$$

$$I_2^- + Fe(CN)_6^{-3} \longrightarrow Fe(CN)_6^{-4} + I_2 \qquad (4)$$

while, more recently, Bøckman and Sandved[20] proposed pre-equilibrium of the type

$$Fe(CN)_6^{-3} + I^- \rightleftarrows Fe(CN)_6I^{-4} \qquad (5)$$

but with no discussion of the nature of the intermediate postulated. There is general agreement that a large salt or ionic strength effect exists.

The oxidation of thiosulfate was studied by Sandved and Holte[21] who noted that the rate was approximately first order in hexacyanoferrate(III) and first order in thiosulfate, but somewhat inhibited by ferrocyanide and accelerated by tetrathionate ion. The proposed mechanism was

$$Fe(CN)_6^{-3} + S_2O_3^{=} \rightleftarrows Fe(CN)_6^{-4} + S_2O_3^- \qquad (6)$$

$$2S_2O_3^- \longrightarrow S_4O_6^{=} \qquad (7)$$

with the ferrocyanide retardation related to its tendency to form "double compounds." The oxidation of sulfite was found to be measurably slow by Singh and Malik,[22] and Grube[23] noted that cyanide was oxidized, and wrote the over-all equation

$$2Fe(CN)_6^{-3} + CN^- + 2OH^- = 2Fe(CN)_6^{-4} + CNO^- + H_2O \qquad (8)$$

The correlation of electron exchange rates with magnetism or number of unpaired electrons would suggest that a first step of the type

$$Fe(CN)_6^{-3} + X^- = Fe(CN)_6^{-4} + X \qquad (9)$$

should be rapid, and be followed by a rapid combination of the radicals X. That this does not occur is evident from the brief review above, and the explanation is probably that in each case such a first step is unfavorable energetically. Thus, using potentials from Latimer[17] and thermochemical data from West[24] and Pauling,[25] the following estimates can be made for the reactions with iodide and cyanide.

$$\begin{array}{lll} & \Delta H \text{ (kcal.)} & \\ HCN(aq) = HCN(g) & 10 & \text{(taken to be the same as for HF)} \\ HCN(g) = H(g) + CN(g) & 97 & \\ H(g) = 1/2\ H_2(g) & -51 & \\ CN(g) = CN(aq) & -\ 2 & \text{(taken to be the same as for NO)} \\ \hline HCN\ (aq) = 1/2\ H_2 + CN(aq) & 53 & \Delta F \text{ (est)} = 49 \text{ kcal.} \end{array}$$

$$Fe(CN)_6^{-3} + HCN = Fe(CN)_6^{-4} + H^+ + CN \qquad \Delta F = 41 \text{ kcal.}$$

$$Fe(CN)_6^{-3} + CN^- = Fe(CN)_6^{-4} + CN \qquad \Delta F = 27 \text{ kcal.} \qquad (10)$$

---

[17] W. M. Latimer, "Oxidation Potentials," Prentice Hall Publishers, Inc., New York, N. Y., 1938.

[18] W. C. E. Higginson, *J. Chem. Soc.*, 1438 (1951).

[19] E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

[20] O. Bøckman and K. Sandved, *Tids. Kjemi Bergvessen*, **20**, 72 (1940); H. B. Friedman and B. E. Anderson, *J. Am. Chem. Soc.*, **61**, 116 (1939); A. V. Kiss, *Rec. Trav. Chim.*, **52**, 289 (1933); C. Wagner, *Z. physik. Chem.*, **113**, 261 (1924).

[21] K. Sandved and J. B. Holte, *Tids. Kjemi Bergvessen*, **20**, 106 (1940).

[22] B. Singh and I. I. Malik, *J. Ind. Chem. Soc.*, **14**, 435 (1937).

[23] G. Grube, *Z. anorg. Chem.*, **84**, 190 (1913).

[24] C. D. West, *J. Phys. Chem.*, **39**, 493 (1935).

[25] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940.

$$\begin{aligned}
&H^+(aq) + I^-(aq) = \\
&\qquad 1/2\ I_2(aq) + 1/2\ H_2(g) && \Delta F = 6.1 \text{ kcal.} \\
&1/2\ I_2(aq) = I(aq) && \Delta F = 16 \text{ kcal.} \\
\hline
&H^+(aq) + I^-(aq) = \\
&\qquad I + 1/2\ H_2(g) && \Delta F = 32 \text{ kcal.} \\
&Fe(CN)_6^{-3} + I^- = \\
&\qquad Fe(CN)_6^{-4} + I && \Delta F = 24 \text{ kcal.} \qquad (11)
\end{aligned}$$

Comparable data are not available for thiosulfate, but Sandved's mechanism cannot be considered as necessarily correct in view of the incomplete analysis of his data. The sulfite oxidation does not fit this pattern. It is noteworthy that these reactions are photocatalyzed; under such circumstances the activation energy for a reaction of type (9) could be supplied, and it is to be expected that the photocatalyzed reaction would proceed through this path.

It was of interest to examine the kinetics of the cyanide oxidation to see if, as would be predicted by the above, the mechanism involved some intermediate other than cyanogen radical. In a previous publication[26] it was noted that two hexacyanoferrate(III) ions were reduced per cyanide ion oxidized, in accord with equation (8), and that the reaction occurred without any decrease in the specific activity of the free cyanide ion. This last observation made it clear that the major product was hexacyanoferrate(II) ion rather than an aquocyanide, and that no intermediate with a different number of coördinated cyanide groups was involved.

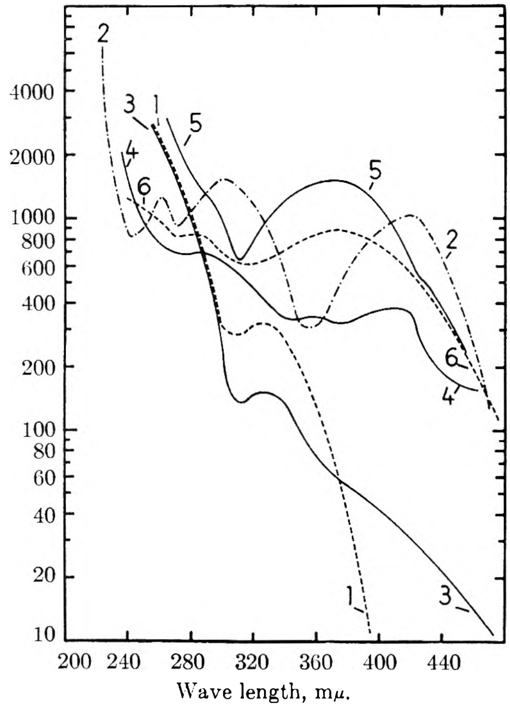


Fig. 1.—Spectra of: 1, hexacyanoferrate (II); 2, hexacyanoferrate(III); 3, pentacyanoaquoferrate(II) in 0.9 M KCl, 0.1 M KCN, 0.1 M HCN; 4. pentacyanoaquoferrate(III) in 1 M KCl; 5, species X. The ordinate scale is 10^3d for the terminal solution of a run with 10^{-3} M hexacyanoferrate(III) in 0.8 M KCl, 0.2 M KCN, 0.2 M HCN; 6, species W. The ordinate scale is 10^3d for 0.45×10^{-3} M C_2N_2 in 1 M KCl, 0.1 M KCN, 0.1 M HCN.

Experimental

Preparation of Solutions.—Potassium cyanide was recrystallized twice from water, and dried under vacuum at room temperature. Potassium hexacyanoferrate(III) and -(II) were twice recrystallized and then air-dried. The purity of these substances was checked by a Liebig titration (for cyanide), iodometrically (for hexacyanoferrate(III)), and by permanganate titration (for hexacyanoferrate(II)). Potassium chloride and nitrate, and hydrochloric and perchloric acids of reagent quality were used without additional purification. The solutions were prepared by weighing out the dry chemicals immediately before their use, with appropriate further dilutions to give the desired concentrations.

Stoichiometry of the Over-all Reaction.—The two to one ratio of hexacyanoferrate(III) to cyanide ion consumed was further confirmed by determining the loss of cyanide under conditions where all the complex was reduced. On the other hand, ammonia was present in amount corresponding to half of the oxidized cyanide, so cyanate is not the sole product. In addition, as will be discussed further below, a small amount of colored by-product is produced which is some type of polymer of cyanogen. No appreciable concentrations of cyanogen as such build up during the reaction, however, since none could be detected (by the Rhodes method[27]) in nitrogen gas bubbled through a reaction mixture.

Rate Measurements.—The rates for solutions 0.1 or more normal in hexacyanoferrate(III) were obtained by iodometric titration of the complex. Zinc sulfate was added to precipitate the cyanide as well as the hexacyanoferrate(II) which was then formed by the addition of potassium iodide. The resulting iodine was determined by thiosulfate titration.

The bulk of the rate measurements were made spectrophotometrically, by means of a model DU Beckman quartz spectrophotometer. The absorption spectra for the two complex ions agreed closely with those reported by Ibers and Davidson.[28] The spectrophotometer sample holder was thermostatted to 0.2°.

From the absorption curves for the two complex ions, the optical density at 420 mμ should be a direct measure of the hexacyanoferrate(III) concentration. Actually a yellow-brown species (species X) appears in the course of the reaction. The absorption spectrum of X is given in Fig. 1, along with the spectra for some of the complex ions of interest. It was at first thought that X might be a pentacyanoaquoferrate, but inspection of the curves in Fig. 1 shows that this is not so. It was further noticed that cyanide solutions at pH 9 developed a yellow-brown color (species Y) on standing overnight, and, if sufficiently concentrated, a brown precipitate. The precipitate is soluble in acid, is non-ferrous; it may correspond to one of the polymerization products of hydrocyanic acid, such as the aminoiminosuccinonitrile described by Hinkel, *et al.*[29] The absorption spectrum of Y was quite different from that of X, and, moreover, the time of buildup of Y was long compared to the reaction times employed.

A possible explanation for species X lay in the observation that a solution 0.1 m in cyanogen at pH 9 also developed a yellow-brown color (species Z), but again the absorption spectrum was unlike that of X. Finally, a rather clear yellowish color was developed by a solution 0.1 M in cyanogen and 0.1 M in potassium cyanide, at pH 9 (species W). The absorption spectrum of W proved to be very close to that of X, as shown in Fig. 1, and it is provisionally assumed that X is therefore some polymer of cyanogen. X is not in equilibrium with cyanogen, since the optical densities followed Beer's law upon tenfold dilution either with 1 M potassium chloride or with 0.1 M potassium cyanide; also the color remained upon addition of enough silver ion to complex all of the cyanide, as well as upon hydrolysis of the cyanogen in 0.5 M base, and upon subsequent silver nitrate titration of the cyanide present. Moreover, X was not oxidized by hexacyanoferrate(III). X therefore appears to be a minor by-product of the reaction, although its presence does indicate that the valence state of cyanogen is present as a reaction intermediate.

Qualitatively, the final amount of X formed was proportional to the initial hexacyanoferrate(III) and cyanide con-

---

[26] A. W. Adamson, J. P. Welker and M. Volpe *J. Am. Chem. Soc.*, **72**, 4030 (1950).

[27] F. H. Rhodes, *Ind. Eng. Chem.*, **4**, 652 (1912).

[28] J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **73**, 476 (1951).

[29] L. E. Hinkel, G. O. Richards and O. Thomas, *J. Chem. Soc.*, 453 (1937).

TABLE II

SUMMARY OF THE RATE STUDIES

Substrate: 0.100 *M* KCN, 0.100 *M* HCN, 0.900 *M* KCl, *p*H 9.00, temperature 25°

Run	Concentrations (moles/liter) × 10^2 $Fe(CN)_6^{-3}$	$Fe(CN)_6^{-4}$	α	$\beta \times 10^3$ (min.)$^{-1}$	Exceptions to above conditions
A	10.0	0	1.07	3.5	0.1 *M* KCN, 0.1 *M* $HClO_4$, *p*H 8.95
B	14.3	0	1.10	5.5	0.129 *M* KCN, 0.0631 *M* $HClO_4$, *p*H 8.95
C	20.1	0	1.10	16.5	0.206 *M* KCN, 0.101 *M*, $HClO_4$, *p*H 9.15
5	1	0	0.83	30.8	
12	0.5	0	.96	23	
9	0.25	0	.96	23	
36	0.5	0.5	.55	7.9	
35	1	0.5	.78	10	
34	1	1	.36	11.7	
49	1	5	.27	4.3	
50	1	10	0	3.7	
51	0.5	10	0	2.4	
56	1	0	1.02	13	37°
59	1	0	0.68	22	3°
57	1	10	0	3	37°
19	1	0	1.00	8.0	0.05 *M* KCN, 0.05 *M* HCN, 0.95 *M* KCl, *p*H 9.00
20	1	1	0.62	5.4	0.05 *M* KCN, 0.05 *M* HCN, 0.95 *M* KCl, *p*H 9.00
21	1	10	0.81	1.1	Same as 19 and 20.
54	1	0	1.05	2.8	0.05 *M* KCN, 0.05 *M* HCN, 0.45 *M* KCl
55	1	10	1.00	0.3	0.05 *M* KCN, 0.05 *M* HCN, 0.45 *M* KCl
52	1	0	0.97	15	0.1 *M* KCN, 0.1 *M* HCN, 0.1 *M* KCl, 0.8 *M* KNO_3
53	1	10	0	3.1	0.1 *M* KCN, 0.1 *M* HCN, 0.1 *M* KCl, 0.8 *M* KNO_3

centrations, inversely so to that of added hexacyanoferrate(II), and much greater at low temperatures than at high temperatures.

The procedure for the spectrophotometric determination of the fraction of hexacyanoferrate(III) unreacted (hereafter denoted by the fraction A/A_0) was based on the above identification of species X, and was as follows. The optical densities were measured at 420 and at 350 mμ. At the latter wave length, the extinction coefficients for the two iron complexes are nearly the same, and as a first approximation, the growth in absorption at 350 mμ was attributed to species X. Then, from the known ratio of $\epsilon_{420}/\epsilon_{350}$ for X, the correction to the optical density at 420 could be made. A second approximation was possible, recognizing the difference in ϵ_{350} for the two complex ions, but usually was not necessary. The A/A_0 values obtained in this manner are also shown in Fig. 2.

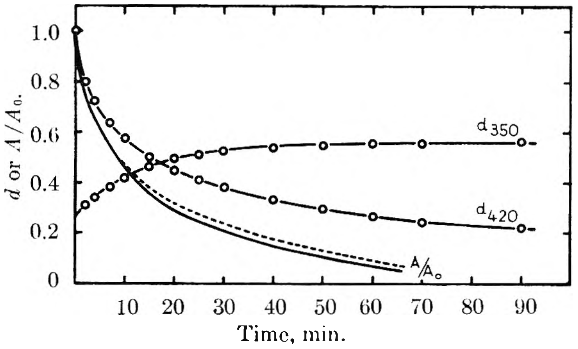


Fig. 2.—Optical densities and A/A_0 values for Run 5.

The runs with added hexacyanoferrate(II) could not so easily be treated; again there was evidence of species X, but the high absorption of hexacyanoferrate(II) at 350 mμ precluded the above procedure. Instead, the simpler assumption was made that the decrease in density at 420 mμ was a linear function of A/A_0. This method gives nearly the same results, as indicated by the dotted line in Fig. 2. Evidently, X accumulates during the reaction in close proportion to the amount of hexocyanoferrate(III) reduced.

Preliminary Rate Experiments.—Preliminary to the data reported in the next section, it was ascertained that the light from the spectrophotometer was insufficient to cause appreciable photochemical reaction, that deaeration of the solutions did not affect the reaction rate, and that neither cyanate nor formamide (a possible hydrolysis product of the cyanide present) affected the reaction. Moreover, no appreciable surface catalysis seemed to be present since comparable results were obtained in large reaction flasks and in the small spectrophotometer solution holders.

Results

The descriptions of the various runs are summarized in Table II; most of them were made with 1 *M* potassium chloride as an ionic strength buffer, and with potassium

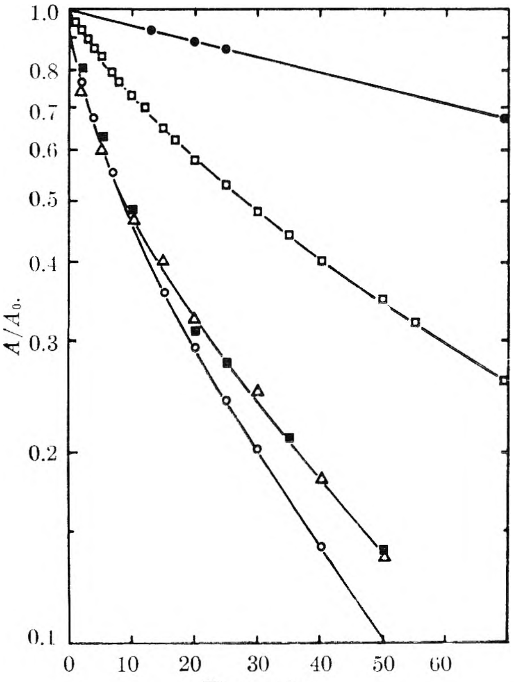


Fig. 3.—Run 5, ○; Run 9, ■; Run 12, △; Run 35, □; Run 49, ●.

cyanide half neutralized with hydrochloric acid to buffer the pH. The values of the fraction of hexacyanoferrate(III) remaining (denoted by A/A_0) were determined as described in the previous section. A few of the runs are shown in Fig. 3, as log A/A_0 *vs.* time plots.

Qualitatively, the results may be summarized as follows: (a) The apparent reaction order was between first and second tending toward first order if added hexacyanoferrate(II) was present. (b) There was an approximately first order retardation by hexacyanoferrate(II). (c) There was first to second order dependance upon total cyanide concentration. (d) The rate was nearly pH independent over the range from 11 to 9, but very small in acid solutions. (e) There was a very small, and possibly negative, temperature coefficient, with some shift in reaction order. (f) There was a large effect of reducing the potassium chloride concentration, and a lesser one of replacing chloride by nitrate or perchlorate. (g) The reaction intermediates did not reach steady state concentrations since, for example, run 36 did not duplicate the second half of run 5.

The complex nature of the reaction, as evidenced by the above points, makes it difficult to write a completely satisfactory mechanism, but certain features would seem to be necessary. First, there must be a pre-equilibrium involving hexacyanoferrate (II) as a product, probably with coefficient unity in order to explain (b) above; moreover, to explain (e), this pre-equilibrium must have a small or negative ΔH, which clearly rules out a reaction of type (9). The second step cannot be of the type suggested by Wagner[20] since this would require the retarded reactions to be second order in hexacyanoferrate(III). The presence of species X (see Experimental) suggests that the oxidation state of cyanogen is present as an intermediate. A mechanism of the following type satisfies these general requirements

$$\mathrm{Fe(CN)_6^{-3}} + 2\mathrm{CN^-} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{Fe(CN)_6^{-4}} + \mathrm{(CN)_2^-} \qquad (12)$$

$$\mathrm{(CN)_2^-} + x\mathrm{H_2O} \xrightarrow[k_3]{} \mathrm{P} + \mathrm{CN^-} \qquad (13)$$

$$\mathrm{Fe(CN)_6^{-3}} + \mathrm{P} \longrightarrow \mathrm{Fe(CN)_6^{-4}} + \mathrm{Q} \qquad (14)$$

Reaction (12) is written with two cyanides to avoid postulating cyanogen radical formation; the ΔF for this reaction should be more negative than that of (10) by an amount of the order of the bond energy of cyanogen, and the enthalpy change should be small enough to be consistent with the small temperature coefficient that is observed. Reaction (13) is written as a partial hydrolysis since alternatives involving radical association or reaction with other species impose the wrong concentration dependencies; moreover, partial hydrolysis at this point is consistent with the observation that of the order of half of the oxidized cyanide appears as ammonium carbonate rather than as cyanate. Species P might be $\mathrm{O{=}C{-}NH_2}$. Reaction (14) is a rapid oxidation of species P.

Application of the stationary state hypothesis to this mechanism leads to the rate expression

$$\ln(A_0/A) - \alpha(1 - A/A_0) = \beta t \qquad (15)$$

where

$$1/\alpha = \frac{k_3}{k_2A_0} + \frac{A_0 + C_0}{A_0}$$

$$\beta = (2k_1'k_3/k_2A_0)\alpha$$

C_0 = concn. of hexacyanoferrate(II) at zero time
$k_1' = k_1(\mathrm{CN^-\ Total})^2$

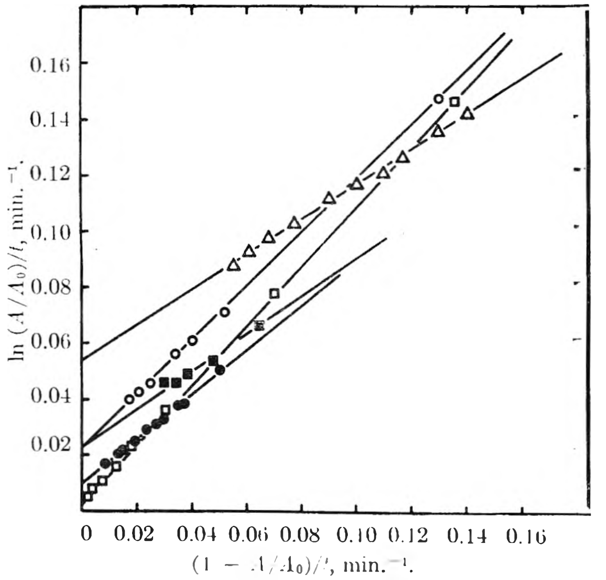


Fig. 4.—Run 9, ○; Run 20, △; Run 54, □; Run 59, ■; Run 35, ●.

Equation (15) represents the data satisfactorily, as shown in Figure 4, in which some of the runs are plotted as $\ln(A_0/A)/t$ *vs.* $(1 - A/A_0)/t$, and a number of values of α and β are given in Table II. As mentioned earlier, however, the data are internally inconsistent with the stationary state hypothesis, and this situation is further evidenced by the failure of the constants α and β to vary from run to run in complete consistency with the proposed mechanism. Thus the variation of α corresponds to a value for k_3/k_2 of about 10^{-4} (mole/liter), while that of β corresponds to one of about 10^{-3} (mole/liter) and to a value of k'_1 of 0.02 min.$^{-1}$, but with major internal trends that make it evident that a more complex behavior is actually present. The independence of the rate upon pH over the range from 12 to 9 suggests that (12) involves forms that are oppositely pH dependent, as, for example, HCN and CN$^-$, or $\mathrm{HFe(CN)_6^{-2}}$ and CN$^-$. The effect of changing total cyanide concentration and of the ionic strength buffer at best can be said to be qualitatively reasonable. Thus Friedman[20] reported that the iodide oxidation was strongly ionic strength dependent, and was faster with chloride present than with nitrate.

Evidently, it would be desirable to solve the non-stationary state equations, but this cannot be done in closed form, and the support for the proposed mechanism remains essentially qualitative. It seems clear, however, that the processes must be of the type postulated and that the slowness of the reaction is not to be attributed to an anomalously slow electron transfer step.

THEORY OF ELECTRON EXCHANGE REACTIONS IN AQUEOUS SOLUTION

BY W. F. LIBBY

Institute for Nuclear Studies and Department of Chemistry, University of Chicago, Chicago 37, Illinois

Received March 13, 1952

The frequencies for the electron exchange in hydrogen molecule ion are calculated for 3d wave functions. It is observed that appreciable frequencies occur at distances of 30 Å. for the simple ion. For higher nuclear charges the distances having given frequencies are reduced roughly inversely with the nuclear charge.

The bearing of the Franck–Condon principle on electron exchange reactions in aqueous solutions as set forth recently by Franck is described and pursued in some detail. The important point is that the hydration energy is not transmissible as rapidly as the electrons. This constitutes a barrier to the reaction. This barrier is reduced by complexing the ions in a firm way so that both valence states are symmetrical and of the same dimensions to within the amplitude of the zero point motions in the ground state. Catalytic effects of small negative ions are to be expected in that they will facilitate the closer approach and consequent sharing of the hydration energies. The possibility that the Franck theory is fundamental to many problems in inorganic and electrochemistry is discussed.

Introduction

The occurrence of electron exchange between aqueous ions has been clearly demonstrated in many cases, and some of the features of the kinetics elucidated. In particular, simple ions like ferrous and ferric,[1] cerous and ceric,[2] and europous and europic[3] appear to exchange slowly enough to be measurable. Certain coördinated ions like manganate and permanganate[4,5] and ferrocyanide and ferricyanide[5-9] appear to exchange immeasurably rapidly. In addition, evidence has been found for a catalysis of the exchange between the simple ions by chloride ion which appears to be first power in the chloride concentration.[1,3]

These apparently somewhat contradictory and amazing results may be explicable on the basis of the ideas of Franck[10a] based on the application of the Franck–Condon principle.[10b] The essential point of the Franck theory is that the hydration atmospheres are unable to move in the time required for the electron transfer. This results in the formation of ions in incorrect environment requiring the later movement of hydration energy from one site to another and constitutes a barrier inhibiting the exchange. The hydration atmospheres of the simple ions probably involve considerable differences in energy and geometric arrangement. In the case of the large coördinated ions like manganate and permanganate and ferro- and ferricyanide the oxygens and cyanides are sufficiently symmetrical so that it is likely that no movement of the oxygen atoms or cyanide groups larger than the natural amplitude of the zero point motion is required in the electron transfer. In addition the energies of hydration of these larger ions are necessarily much smaller because of the size of such ions. For these reasons the barrier is reduced greatly in magnitude by the formation of the highly symmetrical but firmly coördinated ions.

The catalysis by small negative ions such as chloride is probably explicable on the basis of the formation of a linear complex with the chloride between the two exchanging positive ions, this complex being small enough so that the hydration atmospheres of the two ions share a considerable number of water molecules and so reduce the height of the reorientation barrier.

The theory of the problem appears to divide naturally into two parts, the quantum mechanics of the electron exchange itself as treated in vacuum using hydrogen molecule ion as a model, since this case is susceptible of solution; and the application of the Franck–Condon principle to the aqueous solutions. Part A of the present paper treats the first of these and Part B the second.

A. Electron Exchange in the Hydrogen Molecule Ion.—It is easily shown[11] that the energy of separation of the two states for this molecule derivable from any given hydrogen-like wave function is equal to the frequency with which the electron interchanges from one atom to the other divided by Planck's constant, the usual assumptions being made that the two most important constituent states for the molecule are those in which the electron is either on one atom of the other. If we label as in Fig. 1, the exchange frequency is given by

$$h\nu = E_{aa}\frac{2S}{1 - S^2} - E_{ab}\frac{2}{1 - S^2} \qquad (1)$$

where

$$E_{aa} = \int \frac{\psi^2_a}{r_b}\,d\tau \qquad (2)$$

$$E_{ab} = \int \frac{\psi_a\psi_b}{r_a}\,d\tau \qquad (3)$$

and

$$S = \int \psi_a\psi_b\,d\tau \qquad (4)$$

Using 1s wave functions one immediately derives

$$\nu = \nu_0 E^{-R}\left(\frac{2}{R} - \frac{4}{3}R\right) \qquad (5)$$

---

[1] J. Silverman and R. W. Dodson, Brookhaven Quarterly Report BNL-93, p. 65, Oct.-Dec. 1950.

[2] J. W. Gryder and R. W. Dodson, *J. Am. Chem. Soc.*, **71**, 1894 (1949).

[3] D. J. Meier and C. S. Garner, *ibid.*, **73**, 1894 (1951).

[4] H. C. Hornig, G. L. Zimmerman and W. F. Libby, *ibid.*, **72**, 3808 (1950).

[5] N. A. Bonner and H. A. Potratz, *ibid.*, **73**, 1845 (1951).

[6] R. C. Thompson, *ibid.*, **70**, 1045 (1948).

[7] W. B. Lewis, Technical Report No. 19, ONR, "Isotopic Exchange by Electron Transfer Between Complex Ions," M.I.T., Jan., 1949.

[8] J. W. Cobble and A. W. Adamson, *J. Am. Chem. Soc.*, **72**, 2276 (1950).

[9] L. Eimer and R. W. Dodson, Brookhaven Quarterly Report BNL-93, Oct.-Dec., 1950.

[10] (a) *Cf.* E. J. B. Willey, "Collisions of the Second Kind," London, E. Arnold and Co., 1937; and review by K. J. Laidler and K. E. Shuler, *Chem. Revs.*, **48**, 153 (1951); (b) W. F. Libby, Abstracts, Physical and Inorganic Section, 115th Meeting Am. Chem. Soc., San Francisco, Calif., March 27–April 1, 1949.

[11] Eyring, Walter and Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York 1, N. Y., 1944, pp. 192–199.

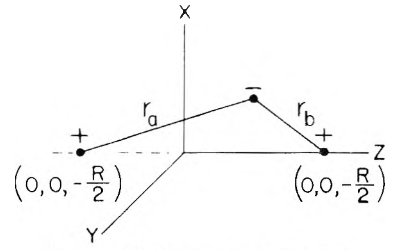


Fig. 1.—Hydrogen molecule ion.

where $\nu_0 = e^2/a_0 = 6.58 \times 10^{15}$ sec.$^{-1}$; and R is measured in units of the Bohr radius 0.5282 Å.

TABLE I

1s EXCHANGE FREQUENCIES FOR H_2^+

R (unit, a_0)	ν/ν_0
5	0.00423
10	5.9×10^{-4}
15	5.7×10^{-6}
20	5.3×10^{-8}
30	4.0×10^{-12}

As shown in Table I and Fig. 2, even the 1s wave function gives very appreciable rates of exchange at distances of 10 Å. and larger.

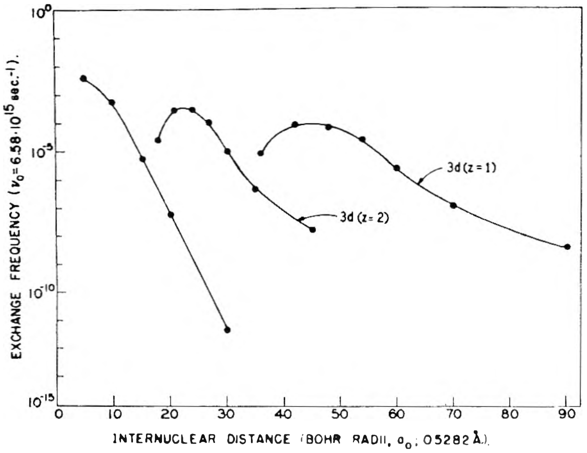


Fig. 2.—Calculated exchange frequencies for hydrogen molecule ion.

Since most of the ions concerned in electron exchange studies have incomplete 3d shells which are probably involved in the actual exchange, we will consider exchange frequencies for various 3d wave functions. In these considerations we will use the generalized hydrogen molecule ion in which the two positive nuclei have charges of $+Ze$, and all of our results will be stated in these terms.

Table II gives the exchange integrals E_{ab} for the five 3d wave functions. The five orbitals are labeled according to the customary nomenclature, where the z-axis is the axis of the molecule as shown in Fig. 1. It is therefore not surprising that the orbital z^2 has the largest value of the exchange integral. We shall therefore restrict our discussion to this orbital. A recent paper by Wohlfarth[12] discusses the exchange integral for 3d states in which the wave function used is the spherically symmetrical one

$$\psi = Ar^2e^{-dr^2} \qquad (6)$$

where A and d are constants. This gives an E_{ab} as shown in Table II under the label w. It might have been preferable to use this wave function as a sort of average for the 3d electrons, but the essential points made below seem not to be seriously dependent on this choice.

TABLE II

EXCHANGE INTEGRALS FOR 3D WAVE FUNCTIONS[a]

3d Orbital	E_{ab} (in units of $h\nu_0Z^2$; $B = RZ/3a_0$)
z^2	$\frac{1}{27}\left[\frac{1}{15}B^5 - \frac{1}{5}B^4 - 3B^3 + \frac{2}{5}B^2 + 3B + 3\right]e^{-B}$
yz, or xz	$\frac{1}{9}\left[-\frac{1}{15}B^4 - \frac{2}{15}B^3 + \frac{1}{2}B^2 + B + 1\right]e^{-B}$
x^2 − y^2	$\frac{1}{9}\left[\frac{1}{15}B^3 + \frac{2}{5}B^2 + B + 1\right]e^{-B}$
xy	$\frac{1}{12}\left[\frac{1}{15}B^3 + \frac{2}{5}B^2 + B + 1\right]e^{-B}$
w	$\left[\frac{1}{625}B^5 + \frac{6}{625}B^4 + \frac{6}{121}B^3 + \frac{7}{45}B^2 + \frac{1}{3}B + \frac{1}{3}\right]e^{-B}$

[a] The author is indebted to Mr. C. E. Weber, who assisted in the evaluation of these and the E_{aa} and S integrals.

The overlap integral S for the 3d$_{z^2}$ wave function is

$$S_{z^2} = (0.0040B^6 - 0.001555B^5 - 0.0556B^4 - 0.09523B^3 + 0.2381B^2 + B + 1)e^{-B} \qquad (7)$$

Table III gives values of this overlap integral for various values of B.

TABLE III

B (units $RZ/3a_0$)	S_{z^2}
1	0.77
5	.16
10	.15
15	.015
20	.00049

Since we shall be mainly interested in discussing the interchanges at distances corresponding to B = 10 or larger, it is clear that the expression for the exchange frequency (Equation 1) can be simplified by dropping the S^2 in the denominator. Even at closer distances one sees that the error so made will not be more than an order of magnitude.

The coulombic integral E_{aa} is

$$E_{aa,z^2} = Z^2\nu_0h\left[\left(\frac{30}{B^5} + \frac{4}{3B^3} + \frac{1}{3B}\right) - 128\frac{e^{-2B}}{B^2}\right] \qquad (8)$$

This expression neglects some terms involving e^{-2B} as a factor and is therefore valid only for values of B of 5 or larger. Finally, substituting in Equation 1, the expression for the exchange frequency is obtained

$$\nu_{z^2} = Z^2\nu_0[e^{-B}(-0.00227B^5 + 0.0138B^4 + 0.196B^3 - 0.0976B^2 + 0.0283B + 0.0918 - 2.03\frac{1}{B} - 54.5\frac{1}{B^2} + 17.0\frac{1}{B^3} + 60\frac{1}{B^4} + 60\frac{1}{B^5}) - e^{-3B}(1.024 \times B^{10} - 0.400B^9)] \qquad (9)$$

For values of B larger than 10 a set of values of ν calculated from Equation 9 is given in Table IV.

Figure 2 shows the values of the calculated exchange frequencies for the 3d$_{z^2}$ and 1s wave functions for various internuclear distances.

B. The Franck-Condon Principle and the Hydration Atmospheres.—Franck[10] has clearly enunciated the principle that electron transfer in

---

(12) E. P. Wohlfarth, *Nature*, **163**, 57 (1949).

TABLE IV

$3d_{z^2}$ ν VALUES[a]

$B(ZR/3a_0)$	ν/ν_0
10	3.4×10^{-3}
12	1.0×10^{-5}
14	9.7×10^{-5}
16	7.1×10^{-5}
18	2.6×10^{-5}
20	2.7×10^{-6}
23.3	1.2×10^{-6}
30	4.4×10^{-9}

[a] The minus sign given for ν for B values larger than about 11 has been dropped because the sign of the energy separation of the two states does not affect the frequency.

aqueous solutions should be inhibited by the relatively longer times required for movement of the heavy water molecules constituting the hydration atmospheres as compared to the transit time for the electron. If the electron transfer proceeds as it does in the hydrogen molecule ions discussed in Part A, these relative times should be roughly equal to the inverse square root of the mass ratio of the water molecule and the electron, about 200. An analogous situation exists in spectroscopy, so we may speak of the application of the Franck–Condon principle to the problem of electron transfer reactions in aqueous solution. More definitely, in the case of the Fe^{++}, Fe^{+++} exchange, the ferrous ion becomes a ferric ion in a ferrous environment, and the ferric ion becomes a ferrous ion in a ferric environment immediately after the electron transfer, the extra energy of hydration being stored at the original site of the ferrous ion and eventually leaking across by the slow type of collisional process which accomplishes heat conduction to the original ferric site. Of course there is no net energy change in the reaction. However, the differences in rates of movement of the electron and the heat mean that the electron must be able to make the transition against a barrier comparable in magnitude to the amount of energy involved in the subsequent slow reorientation of the water molecules to the new charge situation.

One can estimate the magnitude of the barrier in the following way: Imagine the constituent electrical charges which are used to make up the ions to be dissolved in the solution at infinite distances from one another. One then assembles the charges on a sphere of radius r equal to the ionic radius, and in a medium of dielectric constant D, which is nearly 80 for aqueous solutions. The work of assembly is given by the classical expression $Z^2e^2/2Dr$, where Z is the charge of the ion and e is the electronic charge. Therefore, in the case we are concerned with here, the energy barrier $\Delta H\ddagger$ is given by

$$\Delta H\ddagger = \frac{e^2}{2rD}\,[(Z + 1)^2 - Z^2] \qquad (10)$$

or

$$\Delta H\ddagger = \frac{e^2}{2rD}\,(2Z + 1) \qquad (10')$$

in which Z is the charge of the ion having the smaller charge. Of course one realizes immediately that the substitution of the value 80 for D makes this a barrier of rather small magnitude. For example, even if r is as small as 1 Å. the ferrous-ferric barrier would be only 10.8 kcal. per mole. It is clear, though, that so large a value of the dielectric constant is incorrect for distances as small as ionic radii, and therefore the difference in hydration energies will be considerably larger. It seems not unreasonable to suppose that its magnitude may well be 2 or 3 times the lower limit set by the use of the value 80 for D.[13]

It should be pointed out in this connection, however, that the electron in transit has no time for solvation, and we must therefore take an ionization energy not too dissimilar from that for the gaseous problem, as has been done in Part A, though one can justifiably expect that the electron polarizability of the aqueous medium as measured by the square of the refractive index will be effective, and this means about a two-fold reduction of the ionization potential is reasonable. In other words, part of the obstructive action of the molecules and ions which lie between the two exchanging ions is counter-balanced by a lowering of the energy required to remove the electron from the donor ion, and makes the model of the gaseous hydrogen molecule ion somewhat more applicable to the solution case.

Considering the cases in which the exchanging ions are surrounded by fixed coördination spheres as in $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ or in MnO_4^- and $MnO_4^=$, one notices that the Franck–Condon principle probably interposes no barrier, or at least the barrier is likely to be much smaller for the following reasons: The geometries of the ions in these cases is probably so similar in the two valence states that the amplitude of the zero point vibrations is large enough so that a considerable probability of the spatial orientation matching exists in the ground states. Of course these ions are hydrated, but their large size now reduces the hydration energies to a point where this barrier will not be serious, as shown by substitution in Equation 10′ for the ionic radii involved in these cases. We thus arrive at a new principle, *electron exchange can be catalyzed by complexing the exchanging ions in such a way that the complexes are symmetrical providing their geometries are identical to within the vibration amplitudes involved in zero point motion.* This principle of symmetry appears to explain the observed rapid exchange in cases like the iron cyanides and the manganate–permanganate ions.

The principle of symmetry strongly inhibits exchanges between asymmetrical complexes providing the asymmetry involves significant energy differences. For example, it is likely that optical isomers will exchange even though their geometries are different. This would be an interesting point to test experimentally.

The addition of chloride to the ferrous–ferric system causes the exchange to become rapid. It has been shown[1] that the exchange rate is proportional to the first power of the chloride ion concentration. A similar observation has been made for the europous–europic case.[3] It is probable[10b] that small negative ions in general have a catalytic effect proportional to the first power at low concentrations. The reasons for expecting this on the

---

[13] The author is indebted to Professor W. M. Latimer for helpful discussions of this point.

basis of the Franck–Condon principle are as follows: A small negative ion placed between the two positive exchanging ions is a stable configuration and causes the two positive ions to approach one another more closely than they could otherwise, so that their hydration atmospheres are shared to a considerable extent and the dissimilarities thereby are reduced in magnitude. In addition such a linear complex satisfies the principle of symmetry. It is true of course on this theory that the catalytic effect depends on no specific complexing properties of the ions, but purely on the electrostatic forces. It may happen that the particular negative ion chosen will form stable complexes with the positive ions and there may be a catalytic effect due to this. For example, cyanide in the iron system could conceivably catalyze by the formation of the ferrocyanide–ferricyanide pair, but it would also be expected that there be a catalytic effect due to the small cyanide ion itself. In other words, the general catalytic effect of small negative ions is in addition to any other specific complexing effects which may be involved. We see some evidence for this conclusion not only in observed chloride catalytic effects, but also in the observation that it is in perchlorate solutions that the iron exchange occurs most slowly, since perchlorate is a very large ion and can hardly be expected to have the catalytic effect.

It is very probable that the considerations described above apply to all electron transfer reactions, that is, all oxidation reduction reactions in aqueous media. So, for example, we may expect that electrodes will be reversible which involve ions both of which are complexed firmly in such a way that both valence states have the same coördination spheres, *e.g.*, the well known reversibility of the manganate-permanganate, and ferro- and ferricyanide half-cells. In electrode reactions themselves the role of the Franck–Condon principle probably is not minor, but it is by no means obvious as to just what its effects may be. In any case a serious examination of this point may assist in the solution of the time-honored problem of overvoltage.

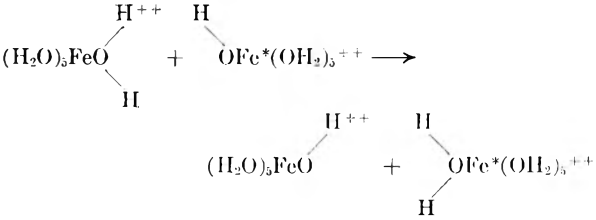
In ordinary oxidation reduction reactions which are exothermic, excited end products may result which satisfy the symmetry principle and which later lose their excitation energy to form the final end products. In other words in an exothermic oxidation reduction reaction energy may be utilized to cross the Franck barrier. For example, the electron transfer may result in the liberation of heat at the site of the reduced ion as well as at the oxidized ion, whereas in exchange reactions the overall heat is of course zero, but hydration energy must move from the oxidized to the reduced ion. The heat is generated only at the site of the oxidized ion.

The difficult question of the permeability of coördination atmospheres for the electron wave function remains. It is obvious that the insulating character will depend on the nature of the molecules or groups constituting the coördination atmosphere. For example, an ammoniated ion may be different from a cyanide complex, the cyanide complex probably being more transmissible because of its ionic character and the ionic resonance states in the cyanide radical which may actually serve as electron conductors. As pointed out earlier, this obstructing effect of the coördination shell and the intervening water molecules is partially counterbalanced by the reduction in the ionization energy by the electronic dielectric constant, which is about 2 for aqueous solutions as calculated by the square of the refractive index. It seems reasonable therefore to expect that the gaseous calculation set forth in Part A is not too inappropriate and that we must expect electron wave functions to reach through several layers of solution as far as exchange and oxidation reduction reactions are concerned. The energies of interaction required are small. The unit ν_0 corresponds to only 27.1 ev., so interaction energies of less than a microvolt are sufficient for rapid exchange. Large complex ions possessing a reducing metallic ion in the center can be rapid reducing agents even though the coördination sphere is of an insulating character.

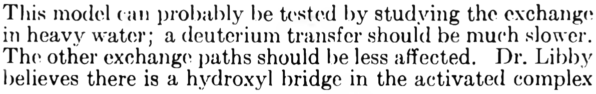
An alternative mechanism for electron transfer reactions which one might consider is the solvation of an electron followed by its subsequent transfer from the solvent to the receiving ion. One knows well that electrons solvate in liquid ammonia, but it seems unlikely that they do to any extent in aqueous solutions since they should reduce water. This mechanism in any case involves an energy barrier equal to the difference between the electronic solvation energy and the ionization potential of the donor ion, and it seems that this will amount to several volts. We therefore believe that such a mechanism is not of great importance in the aqueous electron transfer problems.

DISCUSSION

R. W. Dodson (Brookhaven) and N. Davidson (Cal. Tech.).—An interesting model for the exchange path between Fe^{++} and $FeOH^{++}$ is a hydrogen atom transfer. This may be depicted as



This model can probably be tested by studying the exchange in heavy water; a deuterium transfer should be much slower. The other exchange paths should be less affected. Dr. Libby believes there is a hydroxyl bridge in the activated complex



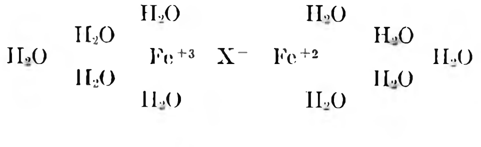
$$(H_2O)_5FeOH^{++} + Fe(H_2O)_6^{++} \longrightarrow (H_2O)_5Fe{-}\overset{H}{O}{-}Fe(OH_2)_5 + H_2O$$

This requires a removal of a water from the hydration sphere of the ferrous ion. It does not predict a large isotope effect.

Norman Davidson (California Institute of Technology).—(1) The heats of activation for the exchange of Fe^{+++}, FeF^{++}, FeF_2^{+}, $FeCl^{++}$, $FeCl_2^{+}$, and $FeOH^{+-}$ with Fe^{++}, and also of CeF^{+++} with Ce^{+++} as well as of $EuCl^{++}$ with Eu^{++} are all about 10 kcal.

Davidson.—(2) Please draw a detailed structure for your idea of the exchange process.

W. F. Libby.—



This picture is very schematic. The essential points are that the transition complex should have a plane of symmetry and should correspond to the displacement of a water molecule from each of the hydration atmospheres of the two ions complexed. The element of symmetry together with the sharing of the hydration atmospheres by the ions and the proximity of the two iron atoms promote the electron exchange, as explained in the paper.

DAVIDSON.—(3) Either one has a symmetrical complex $(H_2O)_5Fe\ X^-\ Fe(OH_2)_5{}^{+4}$, or an unsymmetrical complex, $(H_2O)_5Fe\ X^-\ Fe(OH_2)_5X^{+3}$. The disruption of this complex probably involves a nucleophilic attack by a water molecule in order to maintain the coördinate number of 6 for each cation. That is, the rate-determining step involves the motion of heavy atoms and the Franck–Condon restriction may not be decisive.

LIBBY.—The disruption of the complex constituting the transition state probably will require the assimilation of a water molecule by the iron atom not carrying the X^- away. However, the exchange will have been accomplished as a result of the formation of the symmetrical complex if the theory is correct.

OTTO L. FORCHHEIMER (University of Chicago).—(4) The work of Dwyer and Gyarfas is another excellent example of rapid but measurable exchange between two large ions which presumably have no waters in the inner sphere and are symmetrical. This is good evidence for actual electron exchange.

The work of F. R. Duke lends some support to these ideas. In several cases Duke has found good evidence for complex formation between the reactants in a redox reaction prior to reaction taking place. Furthermore, his results seem to show that certain complexes react much faster than others. The fact that complexes are formed support the bridge picture for electron transfer. The fact that one complex of a particular stoichiometric formula is far more reactive shows that the Franck–Condon requirement of symmetrical configurations must be obeyed. The additional fact that other complexes between reactants reacted only extremely slowly show that a bridge type theory does not mean that electron exchange must take place whenever such a bridge can be formed. Hence the chloride ion inhibition at low Cl^- concentration of the Tl^{III}–Tl^{I} exchange, for instance, does not invalidate Dr. Libby's considerations.

There is no great difference, necessarily, between the Cl^- bridge point of view and the complex ion formation with Cl^- espoused by N. Uri. The formation of a complex ion would, in all probability, mechanistically precede bridge formation. The approach of a second positive ion will be favored, electrostatically, near the position of the chloride ion. The actual bridge model then helps exchange of the electron by the aid to symmetry of forming an actual structure.

F. A. LONG (Cornell University).—(5) The rates of electron transfer between both the ammonia and ethylenediammine complexes of cobaltous and cobaltic ions are very slow (Walker, *et al.*, *J. Chem. Soc.*, Supplement No. 2, 5386 (1949)), much slower than the recently reported rates for transfer between the ordinary hydrated cobaltous and cobaltic ions (Hunt and Bonner, *J. Am. Chem. Soc.*). This fact does not appear to be consistent with Dr. Libby's suggestion that the electron transfer rates will be faster for such highly symmetrical complexed pairs and for the hydrated ions.

LIBBY.—The slow rates of electron exchange for the ammonia and ethylenediammine complexes of cobaltous and cobaltic ions are puzzling unless one should find eventually that the distances between the cobalt and the complexing groups are appreciably different in the two valence states. If this should prove to be so, then of course the theory would predict a slow rate of exchange. (*Cf.* comment of H. C. Brown below).

R. L. WOLFGANG (Brookhaven National Laboratory).—(6) It may be pointed out that the operation of the Franck–Condon principle will usually be less restrictive to electron transfer in non-aqueous solutions than it is in aqueous media. Solvent reorientation in water involves the shifting of strongly dipolar molecules. In a solvent of no dipole moment, reorientation merely involves the rapid displacement of the polarizable electrons. In ammonia, reorientation can probably be achieved largely by the well-known rapid inversion of the molecule. If a suitable system can be found, an investigation of this point would give a good indication of the applicability of the Franck–Condon principle to electron transfer.

S. E. VOLTZ (Houdry Process Corp.).—(7) Although the life expectancy of a linear complex such as Fe^{+++}-Cl^--Fe^{++} would probably be extremely short and the population density at any given time would be exceedingly small, have you considered trying to obtain experimental evidence for its existence by the application of such methods as magnetic susceptibility, mass spectrometry, or dipole moment measurements? These methods have been employed in studies of short-lived free radicals and may prove useful in this case. Of course, negative results would be meaningless in this particular case.

LIBBY.—We have not thought of applying such methods for the detection of the transition state complex, supposing it to be either of too low abundance or detectable by ordinary equilibrium measurements.

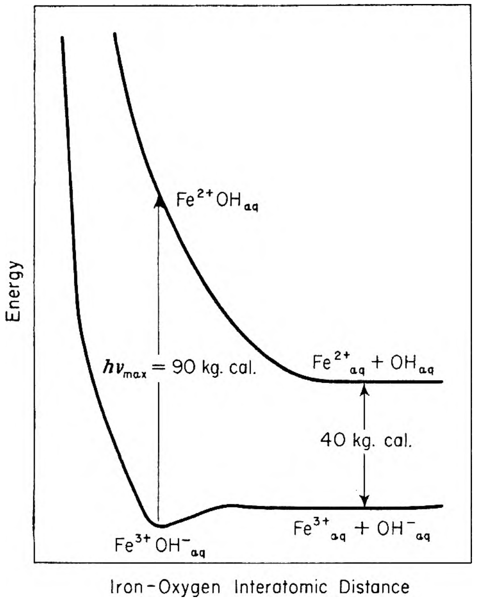
ORLO E. MYERS (Oak Ridge National Laboratory).—(8) Was the MnO_4^-—H_2O exchange experiment conducted in alkaline solution? [I have since learned that the experiment was done in acid, neutral, and alkaline solution, though not as strong as 4 *f* base.] I would like to advance the thought, for whatever it is worth, that your picture of facilitated electron transfer through resonance between nearly equal energy states might be a fruitful approach toward understanding "induced exchange"—which might be a competition between precipitation (to form a non-exchangeable product) and electron transfer during dehydration of the precipitating species, *i.e.*, perhaps the precipitating species assumes a transitory environment which, with the other species, bears the relation of, say, $Fe(CN)_6^{≣}$ to $Fe(CN)_6^{\equiv}$.

LIBBY.—It seems likely that if the theory presented is correct it will have application to heterogeneous electrochemical phenomena, and among these may well be the phenomenon of "induced exchange." One would hope also that many of the classic problems of electrochemistry such as that of the overvoltage of the hydrogen electrode might yield to the theory.

N. URI (University of Chicago).—(9) Would it be feasible to assume that in place of the linear symmetric bridge of the negative ion and the two positive exchanging ions as the electron transfer entity, the latter were to occur between an ion pair complex and a positive ion, *e.g.*, between $Fe^{3+}Cl^-$ and Fe^{2+} ion? The catalytic effect would be understood on the following basis: the hydration energy of the $Fe^{3+}Cl^-$ ion pair complex would be very much different from that of the hydrated Fe^{3+} ion, in view of the total positive charge of +2 of the complex. It is this very large loss of hydration energy which counterbalances the coulombic energy of approximately 400 kcal. (at a distance corresponding to the sum of the ionic radii) and thus makes the ion pair complex formation in solution nearly thermoneutral. The dissimilarity of the hydration energies has thus been largely reduced and perhaps this could in some cases account for the catalytic effect of anions. It is noteworthy that the positive entropy change of ion pair complex formation with ferric ion varies in the order $F^- \simeq OH^- > Cl^- > Br^-$. I would not like to say that this explanation should stand in *all* cases where catalysis of thermoneutral electron transfer has been observed.

LIBBY.—We have been loath to assume that the mechanism advanced by Dr. Uri is important in electron exchange reactions, though it obviously can be important in exothermic oxidation–reduction reactions, where plenty of energy is available to pay for the difference between the states $Fe^{+3}Cl^- + Fe^{+2}$ and $Fe^{+2}Cl^- + Fe^{+3}$. It is true that the hydration barrier would be reduced by the mechanism Dr. Uri suggests, but not so successfully as with the linear symmetric bridged complex $Fe^{+3}\ X^-\ Fe^{+2}$.

URI.—(10) There appears to exist some fundamental difficulty in the interpretation of the lack of considerable activation energy in exothermic electron transfer reactions. This difficulty would arise only if one excludes electron transfer over a distance through the hydration layer by means of tunnels. The following diagram is given to demonstrate the difficulty in such reactions as $Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$ or $Fe^{2+} + Cl \rightarrow Fe^{3+} + Cl^-$.



This diagram illustrates an application of the Franck-Condon principle to "electron transfer spectra" of ion pair complexes [M. G. Evans and N. Uri, *J. Soc. Dyers and Colourists*, **65**, 709 (1949)]. The light energy required to effect electron transfer is by about 40-50 kcal. larger than the corresponding thermal energy in the dissociated and solvated state. It can be shown by a photochemical examination that it is the ion pair complex which, by its photo-excitation, leads to the formation of atoms and free radicals. Due to the constancy of the internuclear distances during the transition the X atom (or radicals) and Fe^{2+} ion in the excited state repel each other. This according to J. Franck [Franck, J. (private discussion)] could largely be accounted for by the penetration of the X atom (or radical) into the hydration layer of the Fe^{2+} ion. The non-equilibrium state of the hydration layer as a whole could also play a certain role. In the foregoing the assumption is made that the interpretation of these spectra as "electron transfer spectra" is fundamentally correct. Were this picture correct and the Franck-Condon principle applied to radiationless transitions, one would expect that, for example, OH radicals or Cl atoms have to climb up an activation hill of 40-50 kcal. before electron transfer occurs. Kinetic evidence indicates that the activation energy is of the order of 2-3 kcal. in these reactions. In addition the interpretation of recent work on promoter and suppressor effects in reactions with Fenton's reagent [N. Uri, *Chem. Reviews*, in press] appears to provide evidence that these reactions do not occur through atom transfer but through electron transfer. Perhaps the answer can be found by Libby's hypothesis that the heat generated at the site of the hydration barrier can be utilized as activation energy.

LIBBY: As Dr. Uri says, the difficulty he envisages arises only if one excludes electron transfer over a distance through the hydration layers as a possibility. It is not clear that one should exclude this as a possibility. In fact as set forth in the paper one knows that electron transfer occurs through the oxygen coördination spheres of manganate and permanganate ions and it is reasonably certain that it occurs through the cyanide coördination spheres of ferrocyanide and ferricyanide ions. If it occurs in these cases it seems not unreasonable that it should occur in other cases such as the one reported by Dr. Uri, providing sufficient energy exists in the reaction to surmount the hydration barrier.

HERBERT C. BROWN (Purdue University).—Professor Libby has indicated that the slow exchange of Co(NH$_3$)$_6^{+++}$ constitutes an exception to the theory he is proposing for electron exchange reactions in solution. Actually, a slight extension of the Franck-Condon principle to cover not only the solvation spheres, but also the coördination spheres, permits the slow exchange of Co(NH$_3$)$_6^{++}$ and Co(NH$_3$)$_6^{+++}$ to be accommodated by the theory.

The ferrocyanide-ferricyanide exchange occurs rapidly. In this case there is little difference in the stability of the two complex ions. Moreover, there is probably little difference in the nature of the iron-carbon bonds in the two instances or in the lengths of these bonds. On the other hand, the two cobalt ammines differ tremendously in stability and it is known that there is a large difference in the lengths of the cobalt-nitrogen bonds in the two complexes. The values 2.5 and 1.9 Å. for Co^{+2}-N and Co^{+3}-N are reported [W. Biltz, *Z. anorg. Chem.*, **164**, 246 (1927)].

Therefore the transfer of an electron to the cobaltic complex would involve the formation of the cobaltous complex with the six cobalt to nitrogen bonds in a highly compressed state. (And *vice versa* for the reverse process.) It appears, then, that rapid exchange should be observed only in those instances in which the complexes derived from the two different valence states do not differ significantly in stability.

From this interpretation it follows that the theory can be generalized to include all ions. In the reaction $(MX_m)^n \rightarrow (MX_m)^{n+1}$ we have two possibilities, where X is joined to M by essentially ion-dipole bonding or by essentially covalent bonding. In the case of the former, the relative stability of the two ions will be determined primarily by the relative magnitude of the ionic charge. Therefore, the solvation sphere about an ion with a +3 charge will always be considerably stable than that about an ion with a +2 charge and the exchange will be slow, as pointed out by Professor Libby. If X is joined to M by essentially covalent bonding, there is no simple relationship of this kind between the stability of the complex and the charge carried by the ion. $(MX_m)^{n+1}$ may be more, less, or equally stable as compared to $(MX_m)^n$. If the two ions do not differ greatly in stability (ferro-ferricyanide, ferro-ferri-phenanthroline complexes), the electron transfer would be fast; if the two ions differ greatly in stability (cobaltous-cobaltic ammines), the transfer would be slow. Thus with this extension the theory proposed by Professor Libby appears capable of accounting for all the present observations on the exchange reactions of complex ions.

CATALYSIS OF THE CEROUS-CERIC ELECTRON EXCHANGE REACTION BY FLUORIDE

By H. C. Hornig and W. F. Libby

Department of Chemistry and Institute for Nuclear Studies, University of Chicago, Chicago 37, Illinois

Received March 13, 1952

The electron exchange reaction between cerous and ceric ions in 6 M nitric acid solution, discovered by Gryder and Dodson, has been studied and its rates at room temperature, 0° and $-14.5°$ observed. The half-time at $-14.5°$ was found to be nearly 4 hours. Working at this low temperature the authors have studied the effects of the addition of small amounts of fluoride and have found a large catalytic action. As little as 10^{-4} mole of KF per liter of solution doubles the exchange rate. This corresponds to 10^{-6} M fluoride, indicating a very efficient catalytic mechanism exists involving fluoride, possibly one in which a single fluoride ion can form symmetrical transition complexes with the fluoride ion being shared by the exchanging cerium ions. It seems possible that a complex involving a single fluoride may be one of the collision partners generating the symmetrical transition complex.

I. Introduction

The electron exchange reaction between cerous and ceric ions in nitric and perchloric acid solution was discovered by Gryder and Dodson.[1] The separation was accomplished by extraction with diethyl ether. The reaction was found to be first order in cerous ion, but of an order between zero and one in ceric ion depending on the concentration of ceric cerium and the nature of the medium. The exchange rate was found to decrease inversely with the square of the H^+ concentration in the HNO_3 medium and with the first power in the perchloric solutions. The activation energy found for the nitric acid solutions was 7.7 kcal./mole.

Evidence has been accumulating for the occurrence of a first order catalysis of electron exchange reactions by simple ions such as chloride, the most marked effects having been found in the case of europous and europic[2] and ferrous and ferric.[3] Since some theoretical basis for this observation has existed[4] based on the general ideas of Franck on the application of the Franck–Condon principle to electron transfer reactions in solution, the present authors have investigated the effect of fluoride in the cerous–ceric system.

II. Experimental

The reagents were made from ceric ammonium nitrate, reagent grade, and hydrated cerous sulfate, both purchased from G. Frederick Smith Company. The radioactive cerium was Ce^{144}, 275 day half-life, obtained from the Isotopes Division, Oak Ridge, Tennessee. The radiocerium was incorporated in the cerous valence state and measurements made on the transfer of radioactivity to the tetravalent state.

The solutions were counted through a thin glass wall solution counter, the 3 Mev. β-radiation of the 17.5 minute Pr^{144} daughter presumably being the principal radiation measured. Care was taken to allow the solutions to sit for at least one hour before measurement.

Measurements were made at room temperature, 0° and $-14.5°$. The lowest temperature bath consisted either of alcohol–water slush or ice–salt water mixture. It is estimated the temperatures were accurate to 1.0°. Some difficulty with the reduction of the ceric by the ether was experienced even at the lowest temperature. Furthermore, at the lowest temperature the formation of two separate layers was barely possible. It appears therefore that this range of temperatures is about the maximum obtainable with this separation method. The diethyl ether used was Mallinckrodt analytical ether. The nitric acid was made by dilution of Baker and Adamson C.P. Reagent Grade concentrated nitric acid.

The solutions were 6 M nitric acid in all cases, and the cerous and ceric ion concentrations were maintained at 2.0×10^{-3} M. After separation the total cerium content of the ether layer was determined by titration and the total cerium content of the aqueous layer similarly determined. It was assumed on the basis of control experiments that cerous cerium was not extracted into the ether layer.

The potassium fluoride solution used for the study of the fluoride catalysis was prepared by heating KHF_2 in a platinum vessel until a constant weight was obtained. This was stored in a desiccator and used to prepare the aqueous KF solutions which were kept in plastic bottles.

III. Results

Table I presents part of the experimental data. The actual points are shown on Figs. 1 and 2, in which the logarithm of the fraction of the exchange remaining to occur is plotted against the time for the various temperatures and fluoride concentrations used. Figure 3 is a plot of the logarithm of the reciprocal of the half times, *i.e.*, the exchange rate *vs.* the reciprocal of the absolute temperature. As is seen, the slope of this line corresponds to an activation energy of 11.7 ± 0.8 kcal. Figure 4 presents the fluoride data for $-14.5°$. It is readily seen that a rapid rise in rate proportional to the total fluoride added is observed. The highest

TABLE I

SUMMARY OF ELECTRON EXCHANGE RATES FOR CEROUS AND CERIC IONS AS CATALYZED BY FLUORIDE

Run	KF Added, M	Temp., °C.	Half-time for exchange (minutes)[a]
1	None	25	11 ± 2
2	None	0	63
8	None	0	64
6	8.4×10^{-4}	0	~2
7	8.0×10^{-4}	0	2.6
9	8.0×10^{-4}	0	3.1
11	8.0×10^{-4}	−14	4.4
12	6.3×10^{-4}	−13.5	5.8
13	4.7×10^{-4}	−14.5	6.8
14	2.5×10^{-4}	−14.5	12.5
19	1.26×10^{-4}	−14.7	26
15	None	−14.6	224
16	None	−14.5	220

[a] Correction for zero time exchange was made graphically. This usually amounted to about 7%.

---

[1] J. W. Gryder and R. W. Dodson, *J. Am. Chem. Soc.*, **71**, 1894 (1949); **73**, 2890 (1951).

[2] D. J. Meier and C. S. Garner, *ibid.*, **73**, 1894 (1951).

[3] J. Silverman and R. W. Dodson, Brookhaven Quarterly Report BNL-93, p. 65, Oct.-Dec. 1950; THIS JOURNAL, **56**, 846 (1952).

[4] W. F. Libby, Abstracts, Physical and Inorganic Section, 115th Meeting Am. Chem. Soc., San Francisco, Calif., March 27–April 1, 1949; THIS JOURNAL, **56**, 863 (1952).

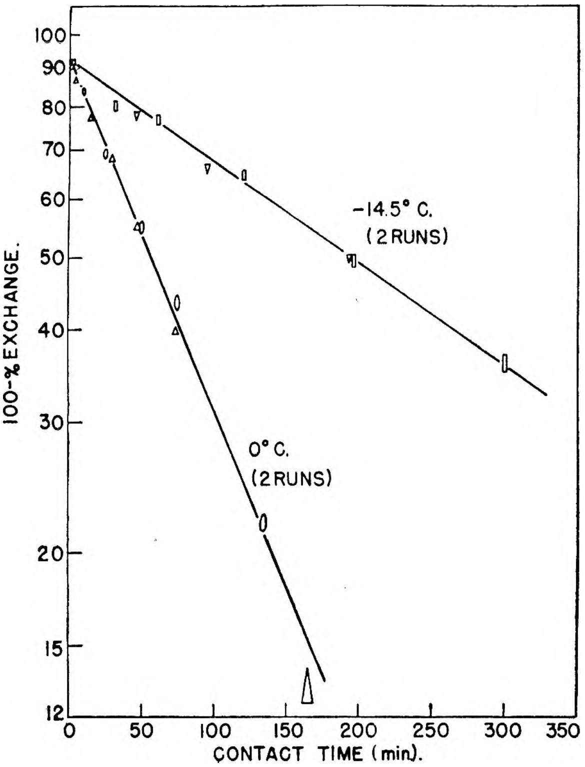


Fig. 1.—Ce(III)/Ce(IV) exchange, temp. effect: 6 M HNO$_3$, 2.0 × 10^{-3} M, Ce(III) = Ce(IV). No salt added.

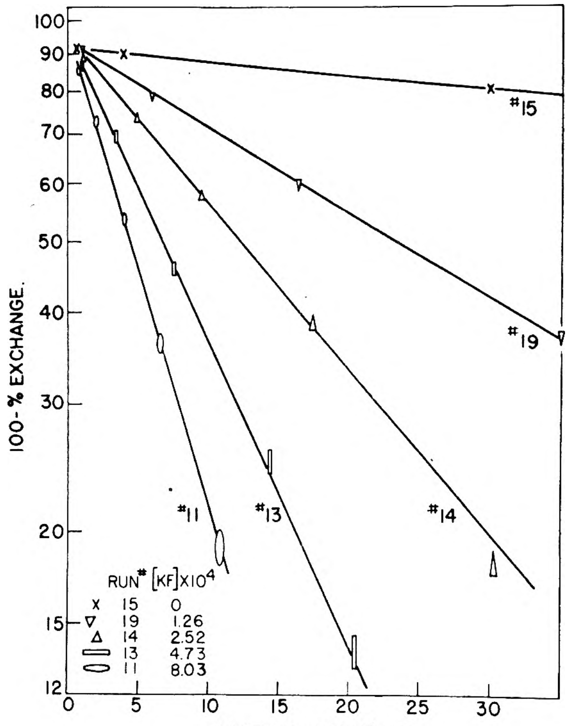


Fig. 2.—Effect of KF on Ce(III)/Ce(IV) exchange rate: −14.5°, 6 M HNO$_3$.

fluoride concentrations may show a slight deviation from linearity. In general it is clear that the original data of Gryder and Dodson have been confirmed and that an additional effect, the catalysis by fluoride, has been found.

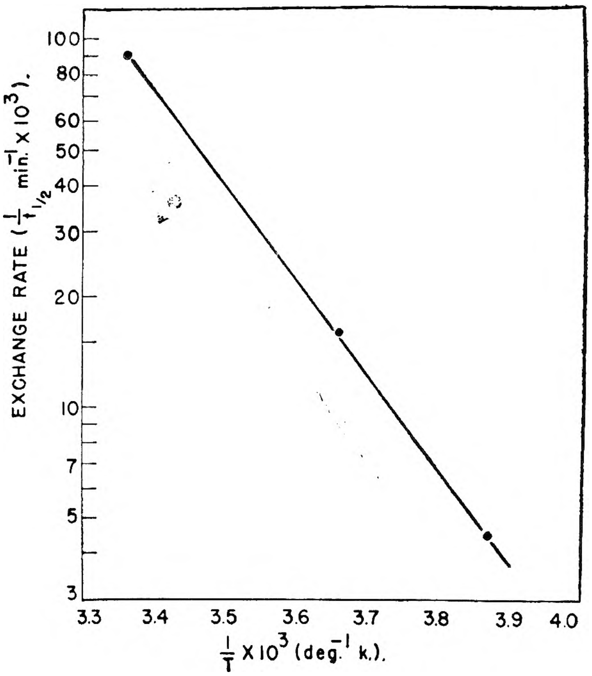


Fig. 3.—Effect of temp. on Ce(III)/Ce(IV) exchange rate: 6 M HNO$_3$, ether extraction, [Ce(III)] = [Ce(IV)] = 2 × 10^{-3} M; ΔH_{act} = 11.7 kcal. mole^{-1}.

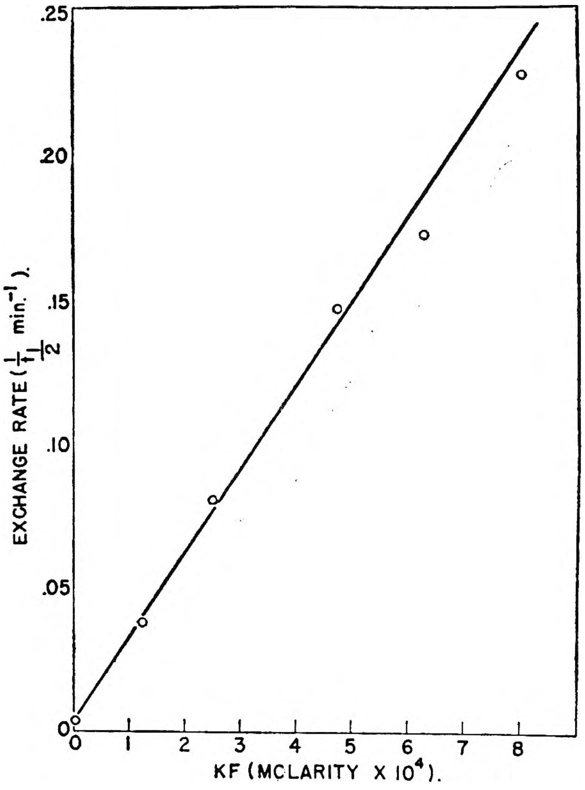


Fig. 4.—Effect of KF concn. on Ce(III)/Ce(IV) exchange rate: −14.5°, 6 M HNO$_3$, ether extraction, [Ce(III)] = [Ce(IV)] = 2 × 10^{-3} M.

IV. Discussion

The dissociation constant for HF is given as 7.2 × 10^{-4} at 25°.[5] Assuming the ionic entropy of fluo-

---

[5] "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," W. M. Latimer, Prentice-Hall Publishers, Inc., 1938.

ride to be -2.3,[5] and the entropy of aqueous HF to be $+41.5$,[5] and neglecting the undoubtedly appreciable effect of the 6 M nitric acid, one calculates the dissociation constant for $-14°$ to be 2×10^{-3}. On this basis the F^- concentration in these solutions can hardly exceed 6×10^{-3} (HF) or 6×10^{-3} times the number of moles of KF added per liter of reacting solution. The proportionality constant is such that the exchange rate appears to double for 3.4×10^{-4} mole of KF added per liter of solution at $-14.5°$. In other words, 2×10^{-6} M fluoride appears to double the rate.

The existence of a first power negative ion catalysis of electron exchange reactions appears to be borne out by experiment. It is difficult to be certain that the magnitudes of the catalytic effects obtained are in agreement with the theoretical[4] model of a transitory collision complex consisting of the two positive ions between which the small negative ion lies for a short time. It seems possible, however, that one of the two reacting ions may form a relatively stable bond with the catalyzing negative ion, in this case F^-, which then is available on collision with the uncomplexed ion of different valence to form the desired symmetrical complex with the negative ion lying on the line joining the two centers of positive charge and bisecting it.

It is to be noted that the chloride catalytic effects are indeed of much smaller magnitude. In general one might expect the larger ions to be less effective.

ISOTOPIC EXCHANGE BETWEEN THE VALENCE STATES OF MERCURY[1]

BY RICHARD L. WOLFGANG AND RICHARD W. DODSON

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York

Received March 15, 1952

The exchange reaction between Hg(I) and Hg(II) in perchlorate solutions has been investigated using picrolonic acid as a precipitant. Complete exchange was found within the time required for separation, in agreement with earlier measurements, and in accord with calculations on the rate of the reversible dismutation of mercurous ion. If an approximately equivalent amount of cyanide is added to the Hg(II), the exchange rate becomes slow and measurable. The order with respect to Hg(I) was found to be 1.08 ± 0.10, with respect to Hg(II) 0.94 ± 0.07. In the range $(CN^-)/(Hg(II))$ 0.5 to 1.8 the rate varies by a factor of two with cyanide concentration, and is not sensitively dependent on pH in dilute acid solution. The specific rate constant for a solution containing equivalent quantities of Hg(II) and cyanide is 0.34 f^{-1} min.$^{-1}$ at 0°, and the experimental activation energy is 14 kcal./mole.

Introduction

The case of exchange between the mercurous and mercuric states of mercury has been studied by Haissinsky and Cottin.[2] These authors found complete exchange between 0.1 *N* solutions of the nitrates at room temperature using a separation by precipitation of Hg_2Cl_2. A somewhat more detailed study was carried out by King[3] on the reaction in perchlorate solution. Employing a method of separation based on precipitation of the chlorides, chromates, or sulfates of mercurous mercury, this author also found complete exchange under all conditions tested. This indicates either that the exchange is fast, or, if it is slow, that exchange is induced by the separation method.

With a view to lessening the second of the above possibilities an organic agent for separating the valence states was sought in this Laboratory. A method in which picrolonic acid was used to precipitate Hg_2^{++} was developed. The technique was applied to the exchange reaction in perchlorate solution and an immeasurably fast exchange found. As will be discussed later this result is in accordance with expectations.

However, when CN^- was present in the reacting solution the rate of exchange became measurable, with either picrolonic acid or chloride as the precipitant for mercurous ion. A study of the kinetics of this reaction was made.

Experimental

Materials.—Radioactive mercuric nitrate (Hg^{203}, 48 d), in nitric acid, of specific activity 210 mc./g. was obtained from the Atomic Energy Commission, Oak Ridge, Tenn. The radiochemical purity of this sample was stated to be greater than 99.9%. A decay curve showed the expected half-life within experimental accuracy. The sample was evaporated with an excess of perchloric acid and diluted. For the purpose of these experiments the resulting solution could be considered as carrier free and was used to introduce activity into the stock reagents.

Mercurous perchlorate was prepared by shaking together for one hour 30 g. of Hg, 23 g. of HgO, 33.3 g. of 60% $HClO_4$ and 50 ml. of H_2O. The resulting solution gave a negative test for mercuric ion. It was diluted to 2 liters and stored in dark bottles in a refrigerator. The reagent was standardized gravimetrically by precipitation of the chloride.

Mercuric perchlorate was prepared by shaking together for one hour 46 g. of HgO, 66.6 g. of 60% $HClO_4$ and 50 ml. of H_2O. The resulting solution gave a negative test for mercurous ion. It was diluted to 2 liters and standardized by titration against KCNS with ferric alum indicator.

A KCN solution was prepared and standarized against $AgNO_3$ and KCNS. A 0.01 *f* solution of picrolonic acid was made from reagent supplied by Eastman Kodak Co.

All chemicals in these preparations and elsewhere in the experiments were reagent or C.P. grade.

Separation Techniques.—It is not feasible to separate Hg(I) and Hg(II) by precipitating the Hg(II) since this causes dismutation of the Hg(I). Accordingly a reagent specific for Hg(I) was sought. Of a number of organic precipitants that were suggested as possibilities by the literature only picrolonic acid[4] was found to be satisfactory. With 10^{-3}–10^{-4} *f* Hg(I) a 0.01 *f* solution of picrolonic acid gives a silky yellow precipitate, which is easily filterable. At 0° precipitation is complete within about two minutes. However to prevent the co-precipitation of Hg(II) the latter must not be present in concentrations greater than approximately 10^{-3}.

When it was discovered that mercuric cyanide complexes exchanged slowly with Hg_2^{++}, a variation of the above separation technique was developed. This consists of quenching the reaction by adding 1–2 equivalents (to Hg(II)) of KCN before the separation by picrolonic acid. The exchange reaction can then be carried out at much lower concentrations if, after this formation of mercuric cyanide complex, more Hg(I) or Hg(II) carrier is added to provide the quantities of material which are necessary for making the precipitation separation. It is recognized that this technique may quite possibly be ineffective since the CN^- added, instead of complexing the Hg(II), might instead largely cause dismutation of the Hg(I), and thus contribute to the exchange reaction rather than quenching it. Thus what is usually true in studies of exchange reactions is especially applicable when this variation of the picrolonic acid precipitation is used: the results are significant if slow exchange is found, but are inconclusive if complete exchange is found.

In the study of the kinetics of the exchange in the presence of CN^-, concentrations of the order of 10^{-2} *f* were used. As indicated previously it is impossible to use picrolonic acid as these concentrations. 0.01 *f* KCl was therefore used to effect a separation by precipitation of Hg_2Cl_2. (It appears that if more concentrated KCl is used the amount of separation induced exchange is increased.)

Procedure.—In each run the appropriate amount of mercurous perchlorate was poured into a reaction vessel already containing the requisite quantities of active mercuric perchlorate, potassium cyanide (if any) and sodium perchlorate (for control of the ionic strength). This was done in a bath thermostatically controlled within ±0.1°. After a suitable time interval either the whole solution or an aliquot thereof was poured into a 2–10 fold excess of 0.01 *f* picrolonic acid or a 50% excess of 0.01 *f* KCl. In the case of exchange runs in the presence of CN^-, additional aliquots were taken over an estimated two to three half-times of the reaction, and another when the exchange was virtually complete, after eight or more half-lives had elapsed.

The precipitate of the mercurous mercury was filtered out on paper, washed, dried, mounted on a cardboard support, covered with cellophane, and counted with a standard mica end-window GM tube. A few milliliters of saturated ammonium nitrate and, if necessary, $Hg(NO_3)_2$ carrier were added to the filtrate and the Hg(II) fraction precipitated with H_2S. This was filtered, mounted, and counted as be-

---

[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] M. Haissinsky and M. Cottin, *J. chim. phys.*, **46**, 476 (1949).

[3] E. L. King, *J. Am. Chem. Soc.*, **71**, 3553 (1949).

[4] A. Martini, *Acta Mikrochim.*, **2**, 296 (1937).

fore. In all cases the sample weight was sufficiently small that any errors due to self-absorption would be negligible.

Calculations.—The fraction exchanged was obtained by comparing the observed activity of the chloride sample with that of the sample taken when the exchange was complete. The sulfide (Hg(II)) fraction was used primarily as a check. The distribution of activity at equilibrium between the two fractions was generally within 3% of the expected value. Half-times were obtained by plotting log (1 − fraction exchanged) against time. Some typical plots of this type are given in Fig. 1.

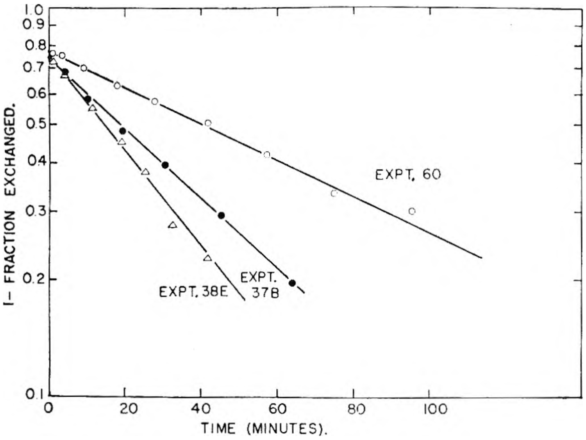


Fig. 1.—Representative curves of original data.

The McKay[5] law gives the time dependence of the fraction exchanged

$$\ln\left(1 - \frac{x}{x_\infty}\right) = -Rt(a + b)/ab \qquad (1)$$

in which x is the activity of the originally inactive material at time t and x_∞ is the same quantity when the exchange is complete. R is the rate of the reaction being studied and a and b are the concentrations of the reactants expressed as the number of equivalents of exchangeable atoms. We have that

$$R = ka^\alpha b^\beta \qquad (2)$$

where α and β are the orders of the reaction with respect to components a and b, respectively. Substituting (2) in (1), inserting the half-time $T_{1/2}$ and taking logarithms we have

$$\ln T_{1/2}(a+b) + (\alpha - 1)\ln a + (\beta - 1)\ln b + \ln k/0.693 = 0 \qquad (3)$$

If now $\ln T_{1/2}(a + b)$ is plotted against $\ln a$ at constant b, the order α is obtained as $\alpha = 1 -$ slope.

Results

Exchange in the Absence of Cyanide.—All experiments carried out on the formally uncomplexed mercury species in perchlorate solution indicated immeasurably fast exchange. The conditions under which some typical runs were made and their results are given in Table I. The experiments were carried out at an ionic strength less than 0.01 and at pH about 3 with the exception of one experiment which was performed in 0.01 f $HClO_4$.

TABLE I

EXCHANGE IN ABSENCE OF CYANIDE

(Hg(I)) $4 \times 10^{-4} f$, (Hg(II)) $5 \times 10^{-4} f$, temp., 0°

Reaction time, sec.	Separation methods	Exchange, %
~2	Picrolonic acid	100
"0"[a]	Picrolonic acid	95
~2	1.9 equivalents (to Hg(II)) of CN^- followed by picrolonic acid	94

[a] In this type of experiment Hg(I) was added to an Hg(II) solution already containing excess picrolonic acid. Note however that two minutes are required for complete precipitation.

Using the variation of the technique described above for very low concentrations a number of experiments were carried out at concentrations less than $10^{-5} f$. Recovery of the activity was usually incomplete, presumably because of surface or impurity effects, but its distribution in the separated fractions always indicated complete exchange. Subject to the reservations previously noted this implies rapid exchange even in the concentration range 10^{-5}–$10^{-6} f$.

Exchange in the Presence of Cyanide.—Preliminary experiments using picrolonic acid showed that in the presence of 1 to 2 equivalents of CN^- per Hg(II) exchange was slow at concentrations of 10^{-3}–$10^{-4} f$. A quantitative study of the kinetics of the reaction was then made in more concentrated solution using precipitation of Hg_2Cl_2 with 0.01 f KCl.

Data on the dependence of the rate of the reaction on the concentration of Hg(I) are given in Table II and graphically in Fig. 2. These experiments were carried out with equivalent quantities of CN^- and Hg(II) present in solution, corresponding formally to the complex $HgCN^+$. The ionic strength was 0.125 f, the temperature 0.0–0.2° and the pH between 2.4 and 2.8 for all runs.

TABLE II

MERCURIC CYANIDE AND MERCUROUS DEPENDENCE IN PERCHLORATE SOLUTION

(Hg(I)), $f \times 10^2$	(Hg(II)), $f \times 10^3$	(CN^-), $f \times 10^3$	$T_{1/2}$, min.	R, moles/l. min.
0.61	7.89	7.89	168	1.41×10^{-5}
1.22	7.89	7.89	107	3.09×10^{-5}
1.22	7.89	7.89	108	3.06×10^{-5}
2.43	7.89	7.89	76	5.4×10^{-5}
2.43	7.89	7.89	62	6.6×10^{-5}
2.43	7.89	7.89	60	6.9×10^{-5}
2.43	7.89	7.89	77	5.4×10^{-5}
2.43	7.89	7.89	62	6.6×10^{-5}
7.30	7.89	7.89	25	1.98×10^{-4}
7.30	7.89	7.89	21	2.35×10^{-4}
7.30	7.89	7.89	24	2.06×10^{-4}
7.30	7.89	7.89	24	2.06×10^{-4}
4.86	7.89	7.89	42	1.12×10^{-4}
4.86	7.89	7.89	33	1.43×10^{-4}
4.86	7.89	7.89	33	1.43×10^{-4}
4.86	15.8	15.8	30	2.76×10^{-4}
4.86	3.16	3.16	30	6.9×10^{-5}
4.86	3.16	3.16	36	5.7×10^{-5}
4.86	1.58	1.58	35	3.0×10^{-5}
4.86	1.58	1.58	35	3.0×10^{-5}

Figure 2 gives a slope of −0.08 ± 0.10 (estimated error) corresponding to an order dependence on mercurous mercury of 1.08 ± 0.10.

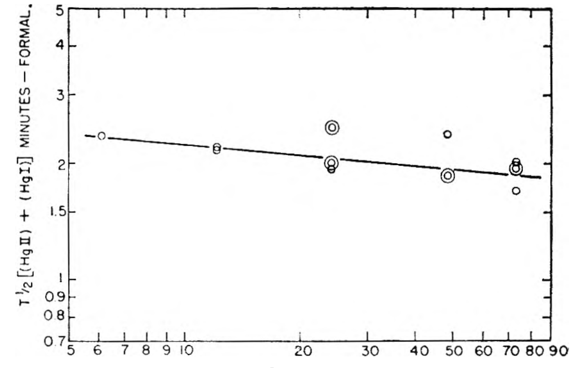


Fig. 2.—Rate dependence on (Hg(I)) (0°, (Hg(II)) = (CN^-) = $7.89 \times 10^{-3} f$, ionic strength 0.125 f).

Data on the mercuric dependence of the reaction are given in Table II and in Fig. 3. In these runs also the ratio (CN^-)/(Hg(II)) was equal to unity, the ionic strength was kept at 0.125, the pH between 2.4 and 2.8 and the temperature between 0.0 and 0.2°.

From Fig. 3 we obtain the order with respect to Hg(II) to be 0.94 ± 0.07. The rate R in moles/l.-min. can thus be expressed by $R = 0.344\,(\mathrm{Hg(II)})^{0.94}\,(\mathrm{Hg(I)})^{1.08}$, at 0°.

---

[5] H. A. C. McKay, *Nature*, **142**, 997 (1938); R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).

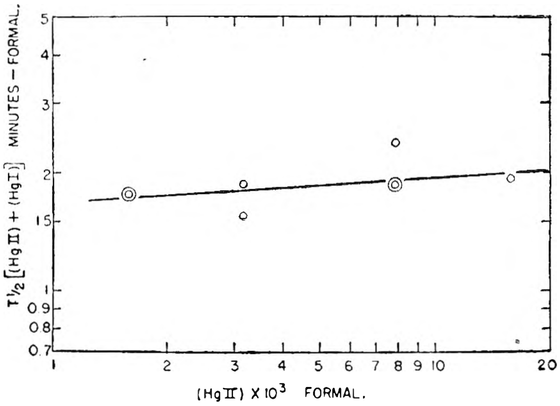


Fig. 3.—Rate dependence on (Hg(II)) (0°, (Hg(II)) = (CN^-), (Hg(I)) = 4.86 × $10^{-2} f$, ionic strength 0.125f).

The dependence of the rate on the number of equivalents of CN^- per Hg(II) added is given in Table III.

TABLE III

DEPENDENCE OF RATE ON CYANIDE

(Hg(II)) 7.55 × 10^{-3} f; (Hg(I)) 4.71 × 10^{-2} f; ionic strength 0.121 f; temperature, 0.0–0.2°; pH ~2.5

(CN^-) formal	(CN^-)/(Hg(II))	$T_{1/2}$, min.	Exchange at zero time, %
3.76 × 10^{-3}	0.50	36	51
5.64 × 10^{-3}	0.75	43	39
7.55 × 10^{-3}	1.00	38	19
7.55 × 10^{-3}	1.00	34	25
8.80 × 10^{-3}	1.17	33	19
9.13 × 10^{-3}	1.21	36	13
1.07 × 10^{-2}	1.42	27	10
1.07 × 10^{-2}	1.42	30	11
1.07 × 10^{-2}	1.42	23	13
1.23 × 10^{-2}	1.63	35	10
1.38 × 10^{-2}	1.83	50	10
1.38 × 10^{-2}	1.83	58	8
1.38 × 10^{-2}	1.83	50	15

The half-times given in Table III were taken from graphs of the type shown in Fig. 1 on the assumption that only one reaction and only one half-time was involved in each experiment. However, in the region where the ratio (CN^-)/(Hg(II)) was 1.2 to 1.8, these plots had some tendency to be concave upward, rather than strictly linear. The method was, however, not sufficiently precise to permit a definite conclusion that more than one component was present. With (CN^-)/(Hg(II)) = 1.83 a significantly longer half-time was observed, indicating the occurrence of a somewhat slower reaction when the relative cyanide concentration is higher. The reaction in the presence of two or more equivalents of cyanide could not be investigated since under these conditions Hg_2^{++} dismutates rapidly and irreversibly to deposit free mercury. In the range that was studied, the most striking result of the experiments is the lack of any considerable sensitivity of the rate on the relative concentration of cyanide.

The percentage exchange at zero time (see Table III) is of interest. (This quantity is given by the intercept of the fraction exchange *vs.* time curve with the zero time ordinate; see Fig. 1.) As would be expected it decreases as the ratio (CN^-)/(Hg(II)) increases to unity. When equivalent amounts of Hg(II) and CN^- are present the zero time exchange averages around 24%, which value can be taken to correspond to the exchange induced by the separation. As (CN^-)/(Hg(II)) is further increased to 1.83 the zero time exchange falls to a value of about 10%.

The pH of the solution in the range 2.7–0.85 was found to have no marked effect on the rate of the exchange reaction, as shown in Table IV.

TABLE IV

EFFECT OF pH ON RATE OF MERCUROUS–MERCURIC EXCHANGE IN PRESENCE OF CYANIDE

(Hg(I)) 2.43 × 10^{-2} f; (Hg(II)) = (CN^-) 7.89 × 10^{-3} f; ionic strength, 0.125 f; temperature, 0.0–0.2°

pH	R, moles/l.-min. × 10^6
2.5–2.7	6.5
1.80	7.0
0.85	6.7

The rate of the exchange shows little dependence on the value of the ionic strength between 0.1 and 2.0 moles/l., as shown by the data in Table V.

TABLE V

EFFECT OF IONIC STRENGTH ON RATE OF MERCUROUS–MERCURIC EXCHANGE IN PRESENCE OF CYANIDE

(Hg(I)) 2.43 × 10^{-2} f; (Hg(II)) = (CN^-) 7.89 × 10^{-3} f; pH 2.5; temperature, 0.0–0.2°

Ionic strength (formal)	R, moles/l.-min. × 10^6
0.125	6.5
0.545	6.5
1.038	6.7
~2.0	5.9

Weiss[6] has suggested that in exchange reactions between different valence states of the same element in aqueous solution dissolved oxygen may be a catalyst. This was not found to be the case in this exchange for the mercurous–mercuric reaction under the conditions employed. Oxygen-free runs were made using the apparatus and technique described by Eimer, Medalia and Dodson.[7] Table VI summarizes the data.

Moderate light intensities had no effect on the rate of the reaction. Experiments carried out in the dark, with some lighting and at sunlight intensity gave half-times within a few per cent. of each other. It was also found that increasing the available surface area by packing the reaction vessel with glass helices had no apparent influence on the reaction.

TABLE VI

EFFECT OF O_2 ON RATE OF MERCUROUS–MERCURIC EXCHANGE IN PRESENCE OF CYANIDE

(Hg(I)) 2.43 × 10^{-2} f; (Hg(II)) = (CN^-) 7.89 × 10^{-3} f; ionic strength 0.125 f; temperature, 0.0–0.2°

Partial pressure of O_2, cm.	R, moles/l.-min. × 10^6
Not controlled (~15)	6.5
< 0.1	5.5
76	5.9

The addition of about 0.01 millimole of colloidal mercury (produced by dismutating a Hg_2^{++} solution with CN^- at the start of an exchange experiment) did not significantly affect the half-time obtained.

The temperature coefficient of the reaction was determined. The relevant data are presented in Table VII and

TABLE VII

TEMPERATURE DEPENDENCE OF THE RATE OF MERCUROUS–MERCURIC EXCHANGE IN PRESENCE OF CYANIDE

(Hg(I)) 2.43 × 10^{-2} f; (Hg(II)) = (CN^-) 7.89 × 10^{-3} f, ionic strength 0.125 f

T, °C.	R, moles/l.-min. × 10^4
0.0	0.65
8.6	1.45
16.9	3.28
24.7	5.5
24.8	5.5
30.5	8.8

---

(6) J. Weiss, *J. Chem. Phys.*, **19**, 1066 (1951).

(7) L. Eimer, A. I. Medalia and R. W. Dodson, *ibid.*, in press.

plotted in Fig. 4. The experimental energy of activation as calculated from Fig. 4 is 14 kcal./mole.

Discussion

Rate of Dismutation of Mercurous Ion.—The dismutation reaction of mercurous ion is thought to have an important bearing on the mechanism of the exchange in the absence of complexing agents. It will be considered in some detail.

We write the equation

$$Hg_2^{++}(aq) \longrightarrow Hg^{++}(aq) + Hg(aq) \qquad (4)$$

where all species are the discrete aquated ions or atoms. To show that this corresponds to an actual reaction it has to be demonstrated that Hg(aq) species actually exists in solution with only a loose coordination sphere of H_2O and does not instantaneously react further to give a new species such as, for instance, $HgOH^-$. Such evidence is given in a paper by Reichardt and Bonhoeffer.[8] These authors spectroscopically examined H_2O in contact with liquid mercury and identified the 2537 Å. line of Hg, apparently broadened only by the electric field of the solvent dipoles. The solubility of Hg in water was found to be of the same magnitude as that of the heavy rare gases.

Consider the cycle

$$\begin{tikzcd}
Hg_2^{++}(aq) \arrow[r, "2"'] \arrow[d, "1"] & Hg^{++}(aq) + Hg(aq) \\
Hg^{++}(aq) + Hg(liquid) \arrow[r] & Hg^{++}(aq) + Hg(g) \arrow[u, "3"']
\end{tikzcd}$$

At 25°, $\Delta H_1° = 862$ cal./mole and $\Delta H_2° = 14{,}535$.[9] It is now assumed that $\Delta H_3°$ is similar to that of the rare gases[10] Xe or Rn. This leads to a value of $\Delta H_3°$ of about -4.8 kcal./mole. Thus for the over-all reaction $\Delta H° = 10.6$ kcal./mole. It follows that $\Delta E° = 10.6$ kcal./mole.

Now the activation energy of a simple unimolecular dissociation reaction is nearly equal to the energy of dissociation,[11] *i.e.*, $E_{exp} = 10.6$ kcal./mole. Furthermore, for a unimolecular reaction, as postulated, the entropy of activation is approximately zero[12]; $\Delta S^{\ddagger} = 0$. Substituting into the absolute rate expression[13]

$$k^{298°} = \frac{eKT}{h} e^{-E_{exp}/RT} e^{\Delta S^{\ddagger}/R}$$

where the symbols have their usual significance, one observes that the reaction rate constant at 298°K. is

$$k^{298°} = 1.9 \times 10^7 \text{ min.}^{-1}$$

which corresponds to an exchange half-time of the order of 10^{-8} minute. Even if the data and assumptions used in calculating E_{exp} or $\Delta S^{\ddagger}$ were in error by 5–6 kcal./mole or 20 cal./deg.-mole., respectively, the process would still only have a half-time of the order of milliseconds.

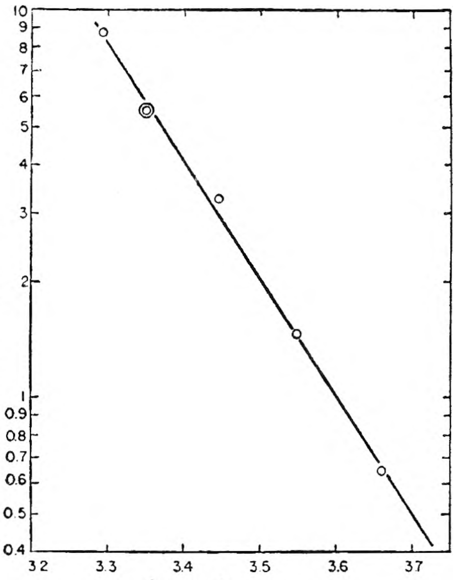


Fig. 4.—Rate dependence on temperature: (Hg(I)) = 2.43 × $10^{-2} f$; (Hg(II)) = (CN^-) = 7.89 × $10^{-3} f$; ionic strength 0.125 *f*.

The Exchange of Uncomplexed Hg_2^{++} and Hg^{++} Ions.—If it is accepted that the dismutation of Hg_2^{++} ion is fast, as is indicated above, then the isotope exchange between the uncomplexed Hg^{++} and Hg_2^{++} ions will be too rapid to measure by any standard technique.

This is in agreement with the experimental findings of complete exchange under all conditions tested. It should again be pointed out, however, that if fast reaction is found in a system of this type it is difficult (if not impossible) to show that this might not have been induced by the separation procedure.

Exchange in the Presence of Cyanide.—Since the exchange rate in the presence of cyanide is slow enough to be conveniently measurable, one concludes, from the arguments given above, that dismutation of mercurous ion dimer is not the rate-controlling step. Neither can the dissociation $Hg_2^{++} = 2Hg^+$ be rate controlling since in this case the Hg(II) dependence would be zero. It seems unlikely that the rate-controlling step is a reaction between Hg(II) and Hg^+ formed in the dissociation since this would lead to a mercurous dependence of 0.5. Furthermore, it is improbable that the rate-controlling step is a reaction between solvated mercury atoms (formed by the dismutation of Hg_2^{++}) and a mercuric cyanide complex, in view of the fact that no large change in rate occurred when the $(CN^-)/(Hg(II))$ ratio was reduced below unity and thus left an excess of Hg^{++} to shift the dismutation equilibrium. Finally mechanisms involving as the limiting factor the dissociation of mercuric cyanide complex can similarly be excluded because of incompatibility with the rate dependence found.

We believe that the present data are most nearly in accord with a mechanism involving as the rate-controlling step reaction between mercurous ion dimer and a cyanide complex of mercuric ion. If this complex is $HgCN^+$, the lack of an appreciable

---

(8) H. Reichardt and K. F. Bonhoeffer, *Z. Physik*, **67**, 780 (1951).

(9) Wendell M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 161, 164, 331.

(10) D. D. Eley, *Trans. Faraday Soc.*, **35**, 1283 (1934).

(11) S. Glasstone, K. S. Laidler and H. Eyring, "The Theory of Rate Processes," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 131.

(12) S. Glasstone, K. S. Laidler and H. Eyring, *ibid.*, p. 296.

(13) S. Glasstone, K. S. Laidler and H. Eyring, *ibid.*, p. 190

effect of ionic strength, even in the range 0.1–2 formal, is surprising; however, it is quite conceivable that the species might be present as neutral HgOHCN, or, what is perhaps more likely in view of the lack of *p*H dependence, as the neutral perchlorate complex $HgCNClO_4$. Further work will be necessary to resolve this point.

The effect of altering the cyanide concentration gives no indication that successive cyanide complexes of mercuric ion are reacting with the mercurous species at greatly different rates, although there is evidence that the $Hg(CN)_2$ may react somewhat more slowly than the complex with a single cyanide.

DISCUSSION

EDWARD L. KING (University of Wisconsin).—If the exchange in the absence of CN^- proceeds by the dismutation mechanism, it is necessary to assume that the complex $HgCN^+$ is not in rapid equilibrium with Hg^{++} and CN^-. If this complex ion equilibrium were established rapidly compared to the rate of dismutation, the complexing of mercury (II) by CN^- would not alter the rate of exchange since the dismutation mechanism corresponds to a rate law: Rate $= k(Hg_2^{++})$. If, on the other hand, the exchange in the absence of cyanide proceeds by mercury atom transfer between Hg_2^{++} and Hg^{++} or by electron transfer between Hg^{++} and Hg^+, the rate of exchange would be diminished by the complexing of Hg^{++} by CN^- even though this complex were labile. The demonstrated presence of cyanide in the activated complex for the exchange in the solutions containing cyanide indicates that the path which dominates in the absence of complexing agent is unimportant (*i.e.*, comparatively slow) in the presence of cyanide.

A. W. ADAMSON (University of Southern California).—1. The authors suggest the process

$$Hg_2^{++}(aq) = Hg^{++}(aq) + Hg(aq) \qquad (1)$$

as being possibly responsible for the rapid exchange between Hg(I) and Hg(II). I would like the authors' comments on the possibility that the dissociation $Hg_2^{++} = 2\,Hg^+$, followed by rapid exchange between Hg^+ and Hg^{++}, provides the exchange path, relative to the following points: (a) The actual activation energy for (1) may be appreciably larger than the estimated over-all ΔH. (b) Higginson (*J. Chem. Soc.*, 1438 (1951)) reports a value of *ca.* 10^{-7} for the dissociation of Hg_2^{++}. Much smaller theoretical estimates (such as Cartledge's) cannot be considered reliable in view of the great uncertainties in the hydration energies of ions in this region of the periodic table.

2. The observation recorded in Table II of the paper, that as little as 0.5 total cyanide to total Hg(II) suffices to make inoperable (for at least half of the Hg(II)) the exchange mechanism acting in the absence of added cyanide, is not explained by the authors. I would like their comments on the following possible explanations. (a) The complexes $HgCN^+$, $Hg(CN)_2$ are formed, with uncomplexed Hg(II) present in amount corresponding to the zero time exchange. It is then necessary to assume that exchange of Hg^{++} with $HgCN^+$ is slow; this seems unlikely, or at least very interesting if true. (b) A complex of stoichiometry Hg_2CN^{+++} is formed, along with $HgCN^+$, etc., and the reduced exchange rate is due to a very low actual concentration of Hg^{++}. The zero time exchange is a catalyzed exchange of these various complex ions. The stoichiometry Hg_2CN^{++} seems improbable. (c) The exchange in the absence of cyanide is catalyzed in some manner that is inhibited by the addition of cyanide to the system.

R. W. DODSON.—1. We see no way to exclude a mechanism of dissociation followed by rapid exchange, nor, on the basis of available data, any particular reason to prefer it.

2. The authors favor the explanation given in 2(a). There seems to be no obvious *a priori* reason for expecting the complex $HgCN^+$ to be labile with respect to exchange with Hg^{++}. This would be an interesting question to look into.

THE KINETICS OF THE OXIDATION OF IRON(II) BY BROMINE

BY PAUL R. CARTER AND NORMAN DAVIDSON

Gates and Crellin Laboratories of Chemistry of the California Institute of Technology, Pasadena, California

Received March 13, 1952

The kinetics of the oxidation of iron(II) by aqueous bromine has been investigated spectrophotometrically at an ionic strength of 1.00 maintained with sodium ions and perchlorate ions. In solutions with $(H^+) = 0.5$–0.8 M, $(Br^-) = 0.05$–0.5 M, $(Fe^{++})_0$ and $(\Sigma\ Br_2)_0 = 10^{-5} - 10^{-4}$ M, $(Fe^{+++})_0 = 0$–10^{-3} M, the rate law is $-d(\Sigma\ Br_2)/dt = k_2(Fe^{++})(Br_3^-)[1 + (k_7(Br^-)(Fe^{+++})/k_3(Fe^{++}))]^{-1}$; $k_2 = 34.0\ (\pm 0.7)$(liter/mole sec.) at 29.8°, 21.8(±0.3) at 20.4°, $k_2 = 10^{7.59(\pm 0.36)}$ exp-$(-8400(\pm 500)/RT)$; $(k_7/k_3) = 0.11(\pm 0.01)$ at 29.8°. The probable mechanism is given by equations (2) and (3). The inhibition by ferric ion is strong evidence for this reaction path and eliminates an alternate path involving iron(IV) as the unstable intermediate. The available thermodynamic estimates give for reaction (2), $\Delta F°_{298} = 8.8$ kcal., $\Delta H°_{298} = 1.0$. In solutions with $(H^+) = 0.1$–0.9 M, $(Br^-) = 1$–3×10^{-3} M, there are additional terms in the rate law, $k_5(Br_2)(Fe^{++}) + k_{14}(HOBr)(Fe^{++})$, for reactions of molecular bromine and hypobromous acid; $k_5 = 0.76(\pm 0.2)$; $k_{14} = 2.1(\pm 0.4) \times 10^4$ at 29.8°. Phosphoric acid catalyzes the reaction; in solutions with $(H^+) = 0.1$–0.7 M, $(Br^-) = 0.2$–0.5 M, $(H_3PO_4) = 0.1$–0.5 M, the main additional rate term at 29.8° is $2.4(\pm 0.4) \times 10^3\ (Br_3^-)(Fe^{++})\ (H_2PO_4^-)$.

The reaction

$$2Fe^{++} + Br_3^- \text{ (or } Br_2) \longrightarrow 2Fe^{+++} + 3Br^- \text{ (or } 2Br^-) \quad (1)$$

is of interest because it presumably proceeds *via* the two one-electron steps

$$Fe^{++} + Br_3^- \underset{k_7}{\overset{k_2}{\rightleftarrows}} Fe^{+++} + Br^- + Br_2^- \quad (2)$$

$$Fe^{++} + Br_2^- \xrightarrow{k_3} Fe^{+++} + 2Br^- \quad (3)$$

involving the formation of the unstable species, Br_2^- (or a bromine atom). The kinetics of the oxidation of iron(II) by aqueous hydrogen peroxide[1,2] and by iodine,[3] and of titanium(III) by iodine[4] indicate that these reactions proceed by analogous mechanisms involving OH radicals and I_2^-. The induction of the isomerization of maleic to fumaric acid by the reaction of dipositive iron with aqueous bromine is evidence for the occurrence of bromine atoms or Br_2^- in reaction (1).[5] Several reactions due to chlorine atoms or Cl_2^- have been induced by the addition of iron(II) to chlorine solutions.[6] Reactions of OH radicals, induced by the addition of dipositive iron to hydrogen peroxide (Fenton's reaction), have been extensively studied.

Several observers have made the qualitative observation that the reactions of aqueous bromine or chlorine with dipositive iron are not "instantaneous."[7-10] We have accordingly found that it is possible to measure the rate of reaction (1) by rapid manual operation of a Beckman spectrophotometer when the reagents are present at concentrations in the range 10^{-3}–10^{-5} M. The kinetic results confirm the reaction path consisting of steps (2) and (3) above, provide some information about the rates of reaction of molecular bromine and hypobromous acid as well as of the tribromide ion, and disprove an alternate mechanism based on the formation of tetrapositive iron as an intermediate.

Experimental

Materials.—Weighed quantities of ferrous ammonium sulfate were dissolved in 1 M perchloric acid. There was less than 2% air oxidation per month of these *ca.* 10^{-3} M Fe^{++} solutions (iron(III) in the solutions was estimated after addition of phosphoric acid by the ultraviolet light absorption of the iron(III)-phosphate complexes).[11] Weighed quantities of sodium bromate were dissolved in an excess of sodium bromide and perchloric acid to give the tribromide ion solutions. Solutions of molecular bromine, prepared by the addition of the C.P. liquid to mixed sodium perchlorate–perchloric acid solutions, were standardized iodometrically. C.P. sodium bromide was dissolved in distilled water and a small amount of bromine was added. Excess bromine was boiled away and the solution filtered. Iron(III) perchlorate ($Fe(ClO_4)_3 \cdot 9H_2O$) was prepared by dissolving ferric chloride in 60% perchloric acid and fuming. After two recrystallizations from water, the product was free of chloride ion. Solutions in perchloric acid were standardized iodometrically.

Sodium perchlorate was prepared by neutralization of C.P. sodium bicarbonate with perchloric acid. Since sodium perchlorate is frequently used as an inert salt to adjust ionic strength, it is important to note that the G. F. Smith Co. anhydrous sodium perchlorate was unsatisfactory for our studies in that 0.5 M solutions were about 10^{-4} N in oxidizing impurities that reacted with Fe^{++}.

Procedure.—About 1.5 ml. of an iron(II) solution was rapidly discharged into a 1-cm. path length, glass stoppered, quartz cell containing an equal volume of a bromine solution, or *vice versa*. The iron(II) solution was added from a calibrated pipet driven by a hypodermic syringe. The pipetting gave almost complete mixing, but the cell was stoppered and shaken for a few seconds to ensure mixing, and then placed in a thermostated cell compartment of a Beckman model DU spectrophotometer. The first optical density reading was usually obtained about 24 seconds after mixing, and the half-time of a typical experiment was about 3 minutes. The response time of the spectrophotometer to small changes in optical density is less than a second.

Extinction Coefficients.—The formal extinction coefficients, $\epsilon = D/(\Sigma\ Br_2)$, of bromine solutions, as measured in this research, are listed in Table I.

TABLE I

FORMAL EXTINCTION COEFFICIENTS, ϵ, OF BROMINE AT 29.8° IN 0.5 M $HClO_4$, 0.5 M NaBr ($\epsilon = (1/cl)\log_{10} I_0/I$)

λ (mμ)			350	340	330	320	310	300
ϵ (liter/mole cm.) $\times 10^{-3}$			0.97	1.48	2.70	4.21	6.62	10.2
λ	290	280	270	265	260	255	250	245
ϵ	15.9	24.3	31.8	32.2	29.3	23.7	16.7	10.8

---

(1) F. Haber and J. Weiss, *Proc. Roy. Soc. (London)*, **A147**, 332 (1934).

(2) J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946); W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *ibid.*, **47**, 462 (1951).

(3) A. V. Hershey and W. C. Bray, *J. Am. Chem. Soc.*, **58**, 1760 (1936); this paper gives references to the many significant earlier investigations of this reaction.

(4) C. E. Johnson and S. Winstein, *ibid.*, **73**, 2601 (1951); D. M. Yost and S. Zabaro, *ibid.*, **48**, 1181 (1926).

(5) F. Wachholtz, *Z. Elektrochem.*, **33**, 545 (1927).

(6) H. Taube, *J. Am. Chem. Soc.*, **65**, 1876 (1943); **68**, 611 (1946).

(7) P. Farrington, Ph.D. thesis, California Institute Tech., 1950.

(8) H. von Halban and H. Eisner, *Helv. Chim. Acta*, **18**, 724 (1935).

(9) R. N. J. Saal, *Rec. trav. chim.*, **47**, 73 (1928).

(10) A. W. Francis (*J. Am. Chem. Soc.*, **48**, 655 (1926)) concluded, on the basis of competition experiments with organic reducing agents, that the rate constant for the reaction between aqueous $FeSO_4$ or $FeCl_2$ and Br_2 is *ca.* 4×10^4 (liters/mole sec.). This number is a factor of 10^2 greater than the rate constant obtained by us.

(11) P. R. Carter and N. Davidson, to be published.

The data of Griffith, McKeown and Winn[12] for the dissociation constant of the tribromide ion, when extrapolated to $\mu = 1.0$ and $T = 29.8°$, give $K_D = (\mathrm{Br_2})(\mathrm{Br^-})/(\mathrm{Br_3^-}) = 0.0615$ mole/liter. The molecular extinction coefficients of the tribromide ion are therefore 1.123 times the ϵ's of Table I. (The contribution of molecular bromine to the light absorption listed in Table I is negligible.) The formal extinction coefficients of bromine in bromide solutions at 20.4° agreed with those calculated from the above data using $K_D = 0.0570$. The formal extinction coefficient of iron(III) in 0.5 M NaBr–0.5 M HClO$_4$ was determined as 275. This value was used in correcting the observed optical densities for the small contribution due to iron(III) formed in the reaction. The molecular extinction coefficient of bromine in 0.5 M HClO$_4$ and 0.5 M NaClO$_4$ at 452 mμ was measured as 93.6. The absorption spectra of iron(III) in phosphoric acid will be reported later.[11]

Results and Discussion

All reaction rates were measured at the constant ionic strength of 1.0, maintained with sodium ions and perchlorate ions, after the desired acidity and bromide ion concentration were selected. The kinetic results for any particular run at a constant acidity and bromide ion concentration conformed to the rate law

$$-d(\Sigma\mathrm{Br_2})/dt = k(\Sigma\mathrm{Br_2})(\mathrm{Fe^{++}}) \qquad (4)$$

where $(\Sigma\ \mathrm{Br_2})$ is the total (formal) concentration of bromine. Figure 1 displays the results of a typical run.

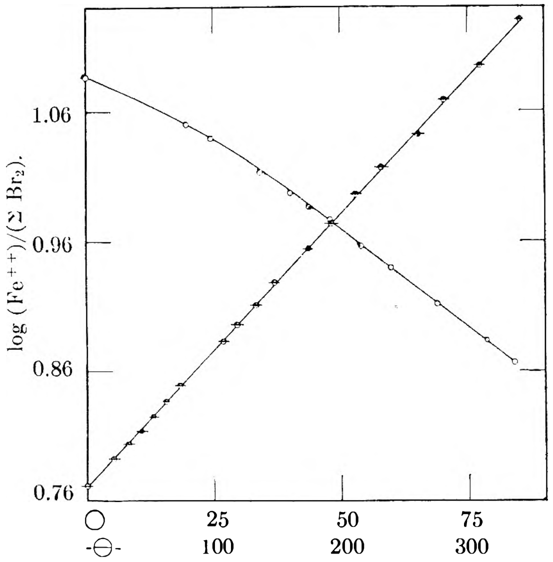


Fig. 1.—Rate of reaction of iron(II) with aqueous bromine: -⊖-, 20.4°, 0.5 M NaBr, 0.5 M HClO$_4$, $(\mathrm{Fe^{++}})_0 = 1.88 \times 10^{-4}$ M, $(\Sigma\ \mathrm{Br_2})_0 = 3.18 \times 10^{-5}$; M ○, 29.8°, 0.5 M HClO$_4$, 0.5 M NaClO$_4$, $(\mathrm{Br^-})_0 = 1.02 \times 10^{-3}$ M, $(\mathrm{Fe^{++}})_0 = 4.15 \times 10^{-3}$ M, $(\Sigma\ \mathrm{Br_2})_0 = 3.39 \times 10^{-3}$ M; the vertical coördinate is 1 + log $(\mathrm{Fe^{++}})/(\Sigma\ \mathrm{Br_2})$ for this run.

The Uninhibited Tribromide Ion Reaction.—The pertinent results are collected in Table II. At a fixed bromide ion concentration, the constant k is independent of the initial concentration of reactants. Experiments with small amounts of added sulfate showed that the amount added as ferrous ammonium sulfate did not affect the rate; check experiments, not listed here, showed that there was no photochemical reaction due to the light of the spectrophotometer. Deaeration of the solutions with nitrogen did not affect the results. The rate constants are independent of hydrogen ion concentration over the limited range studied. The values of k_1 in Table II are calculated from k by the relation $k_1 = k\ (1 + K_D/(\mathrm{Br^-}))$, where K_D, the dissociation constant of the tribromide ion at $\mu = 1.0$, is taken as 0.0615 at 29.8° and 0.0570 at 20.4°. The constancy of k_1, when the bromide ion concentration is varied from 0.05 to 0.5 M, shows that, in this concentration range, the tribromide ion is the reactive bromine species.

Table II

Results at $(\mathrm{Br^-})$ = 0.05, 0.2 and 0.5 M, 29.8 and 20.4°

All runs were at $\mu = 1.00$, maintained with Na$^+$ and ClO$_4^-$; all runs were at $(\mathrm{H^+}) = 0.50$, unless otherwise noted; spectrophotometric observations at $\lambda = 300$ mμ.

$(\mathrm{Fe^{++}})$	$(\Sigma\mathrm{Br_2})$	$(\mathrm{Br^-})$	k	k_1
moles/liter × 10^5		moles/liter	liters/mole sec.	
		$T = 29.8°$		
6.27	2.15	0.479	29.6	33.4
6.27	4.30	.483	30.5	34.4
7.42	5.62	.483	30.6	34.5
12.54	2.27	.479	29.6	33.4
12.54	4.56	.483	29.6	33.3
12.54^{a,e}	4.58	.483	30.4	34.3
12.54^{b,e}	4.48	.483	31.0	34.9
	for $(\mathrm{Br^-})$ = 0.5, k_1 (av.)		= 33.8 ± 0.5	
6.27	5.36	0.196	26.5	34.8
6.27^c	5.10	.196	25.3	33.3
12.54^d	3.92	.209	26.6	34.4
	for $(\mathrm{Br^-})$ = 0.2, k_1 (av.)		= 34.2 ± 0.7	
12.54	12.93	0.0498	14.9	33.1
18.80	12.54	.0498	15.7	35.1
25.09	12.89	.0498	15.3	34.2
	for $(\mathrm{Br^-})$ = 0.05, k_1 (av.)		= 34.1 ± 0.9	
		$T = 20.4°$		
6.27	3.18	0.500	19.0	21.2
6.27^e	5.14	.500	18.5	20.7
12.54	3.21	.500	19.4	21.7
12.54	5.10	.500	19.7	22.0
18.81	3.18	.500	19.6	21.9
18.81	5.10	.500	19.7	22.0
			k_1 (av.) = 21.8 ± 0.3	

^{a} $(\mathrm{SO_4^{=}}) = 6.6 \times 10^{-4}$ M. ^{b} $(\mathrm{SO_4^{=}}) = 1.33 \times 10^{-3}$ M. ^{c} $(\mathrm{H^+}) = 0.80$ M. ^{d} $(\mathrm{H^+}) = 0.65$ M. ^{e} Excluded from average.

The values of k_1 at 20.4° (21.8 ± 0.3) and 29.8° (34.0 ± 0.7) have been used to derive the equation

$$k_1 = 10^{7.59(\pm 0.36)} \exp\left(-8400\ (\pm 500)/RT\right)$$

The errors quoted are probable errors, not estimated safe limits of errors.

Inhibition by Ferric Ions.—The results of the previous section are consistent with the reaction path of equations (2) and (3) and the assumption that $k_3 \gg k_2$. (A mechanism composed of reaction (2) followed by $\mathrm{Br_2^-} + \mathrm{Br_2^-} \rightarrow \mathrm{Br_3^-} + \mathrm{Br^-}$ is consistent with the rate data, but implausible.) If this be true, the rate constant, k_1, of Table II is equal to k_2. Assuming that ΔF and ΔH for the reaction $1/2\ \mathrm{Br_2} \rightarrow \mathrm{Br}$ are the same in solution as in the gas phase, one calculates for the reactions[13]

---

[12] R. D. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

[13] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C.; Series I, Table 11-1, June 30, 1948; Table 47-1, June 30, 1949.

		ΔF°_{298}	ΔH°_{298}
(5′)	$Fe^{++} + Br_2 \longrightarrow Fe^{+++} + Br^- + Br$	12.0	4.2
(6′)	$Fe^{++} + Br \longrightarrow Fe^{+++} + Br^-$	−26.6	−41.8

The thermodynamic data for reactions (2) and (3) will be slightly different from those for reactions (5′) and (6′) because of the association of Br_2 and Br with Br^- to give Br_3^- and Br_2^-. There is evidence[14] that the dissociation constant for the reaction, $Br_2^- \rightarrow Br^- + Br$, is about 10^{-4}, *i.e.*, substantially smaller than the dissociation constant of Br_3^-. We accordingly estimate

		ΔF°_{298}	ΔH°_{298}
(2)	$Fe^{++} + Br_3^- \underset{k_7}{\overset{k_2}{\rightleftarrows}} Fe^{+++} + Br^- + Br_2^-$	8.8	1.0
(3)	$Fe^{++} + Br_2^- \xrightarrow{k_3} Fe^{+++} + 2Br^-$	−21.2	−36.4

At a finite ionic strength, the ΔF's for both reactions (2) and (3) would be more negative than the values given. The data suggest that reaction (3) is likely to be a very fast reaction but that the rate-determining reaction (2) is a difficult one that should be readily reversed, *i.e.*, that Br_2^- can reduce Fe^{+++}. If k_7 the rate constant for the reverse of reaction (2) is of comparable magnitude to k_3, inhibition by Fe^{+++} should be observed. In experiments with no added iron(III), there was no evidence for deviations from linearity of the plots of log $(Fe^{++})/(\Sigma\ Br_2)$ *vs.* time (Fig. 1) over the first 50–60% of reaction where the data were usually taken. Experiments with added initial iron(III) are recorded in Table III. The maximum iron(III) concentration that can be used is limited because of the light absorption by this ion. The predicted rate law when reaction (2) is assumed to be reversible is

$$-\frac{d(\Sigma Br_2)}{dt} = k_2\,(Fe^{++})(Br_3^-)\,\frac{1}{1 + \dfrac{k_7(Fe^{+++})(Br^-)}{k_3\,(Fe^{++})}} \quad (8)$$

The quantity k in the table is the empirical rate constant defined by equation (4); the quantity k_1' is given by $k_1' = k\,(1 + K_D/(Br^-))$. According to the formulation above, $k_1' = k_2/1 + k_7(Fe^{+3})(Br^-)/k_3(Fe^{+2})$. The concentration of Fe^{+3} was essentially constant during the course of the reactions; an average value of (Fe^{++}) was used in calculating $k_7(Br^-)/k_3$.

TABLE III

REACTION RATES WITH ADDED IRON(III) AT 29.8°, (H^+) = 0.50, μ = 1.0

(Br^-)	$(Fe^{++})_0 \times 10^5$	$(\Sigma Br_2)_0 \times 10^5$	$(Fe^{+++})_0 \times 10^4$	k	k_1'	$k_7(Br^-)/k_3$
0.50	12.54	2.18	2.43	26.5	29.8	.060
	12.54	2.19	4.86	24.8	27.8	.049
	12.54	2.38	9.72	20.2	22.7	.057
			$k_7\,(Br^-)/k_3$ (av.) =			0.055
		Preliminary experiments				
0.50	5.94	4.40	0.0	38.9	44.1	. . .
	5.94	4.40	1.14	33.4	37.9	0.057
	5.94	4.40	6.52	21.7	24.6	0.054
	5.94	4.40	9.78	18.8	21.3	0.049
0.05	17.99	6.60	0.0	19.7	43.6	. . .
	17.99	10.74	0.0	18.7	41.4	. . .
	7.50	5.76	12.20	20.1	44.4	×
	7.50	10.41	12.20	20.4	45.1	×
	17.99	6.16	7.36	18.8	41.6	×
	17.99	10.55	7.36	19.8	43.8	×

Included in Table III are a set of experiments performed in the initial stages of the investigation when the techniques for making up the reagent solutions were different from those finally adopted and when a clock, later discovered to be unreliable, was used. The values of k_1 for a rather large number of runs made at that time without added Fe^{+3} were in the range 41–44, about 33% higher than the values obtained later. The activation energy and the dependence of rate on bromide ion concentration were given correctly by these experiments. The experiments of this set in Table III at (Br^-) = 0.50 *M* give the same inhibition by iron(III) as was obtained in the later, more reliable, experiments. We therefore believe that the earlier experiments correctly show that there is no inhibition by iron (III) when (Br^-) = 0.05 *M*. The maximum predicted decrease in rate is about 12%, which would not be detected in these rather inaccurate experiments. The observed value of $k_7(Br^-)/k_3$ implies that, in the experiments with no added iron(III), there would be no observable decrease in rate for the first 50% of the reaction due to iron(III) formed.

We conclude therefore that equation (8) quantitatively predicts the effect of the ferric–ferrous ratio on the rate; and that the prediction as to the effect of bromide ion is consistent with the data available.

Reaction (2) can, of course, be written as

$$Fe^{++} + Br_3^- \underset{k_7'}{\overset{k_2}{\rightleftarrows}} FeBr^{++} + Br_2^- \qquad (2')$$

In the available range of bromide ion concentrations, $FeBr^{++}$ is largely dissociated into Fe^{+++} and Br^-($K_{FeBr} = (FeBr^{++})/(Fe^{+++})(Br^-) \cong 0.5$),[15] so that this mechanism is kinetically indistinguishable from the one used here. According to this formulation, $(k_7'/k_3) = 0.27$; the species Br_2^- oxidizes Fe^{++} four times as fast as it reduces $FeBr^{++}$. If may be recalled that Taube[16] has adduced evidence for the reduction of iron(III) by Cl_2^-. The analogous reduction of iron(III) by I_2^- is a step in the reaction between iron(III) and iodide ion.[3]

An alternate mechanism for the oxidation of iron(II) by bromine involves iron(IV) as the reaction intermediate.

$$Fe^{++} + Br_3^- \underset{k_{10}}{\overset{k_9}{\rightleftarrows}} FeBr_3^+ \qquad (9)$$

$$FeBr_3^+ + Fe^{++} \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} 2Fe^{+++} + 3Br^- \qquad (11)$$

This mechanism predicts inhibition by added bromide ion unless it be supposed that iron(IV) exists as $FeBr_3^+$. To explain the observed inhibition by iron(III), one can assume that reaction

---

[14] H. Taube, *J. Am. Chem. Soc.*, **70**, 3928 (1948).

[15] E. Rabinowitch and W. Stockmayer, *ibid.*, **64**, 335 (1942).

[16] H Taube and I. L. Hochhauser, *ibid.*, **69**, 1582 (1947).

(11) is reversible. The equilibrium constant for the over-all reaction (1) is then $K_1 = k_9k_{11}/k_{10}k_{12}$ and the predicted rate law is

$$-\frac{d(Br_3^-)}{dt} = \frac{k_9(Fe^{++})(Br_3^-)}{1 + \frac{k_{10}}{k_{11}(Fe^{++})}}\left(1 - \frac{(Fe^{+3})^2(Br^-)^3}{K_1(Fe^{+2})^2(Br_3^-)}\right) \tag{12}$$

This relation allows for inhibition by iron(III) only insofar as the over-all reaction (1) is reversible; since $K_1 \sim 10^9$, negligible inhibition by iron(III) is predicted by the iron(IV) mechanism in our experiments. The observed inhibition therefore eliminates the iron(IV) mechanism for the oxidation of iron(II) by tribromide ion. It was not possible for Bray and Hershey to eliminate the iron(IV) mechanism for the oxidation–reduction reactions in the iron–iodine system because, in this case, K is much smaller and the over-all reaction is in fact reversible.

Rate studies at low bromide ion concentrations where tribromide ion is largely dissociated, were made to investigate possible reactions of hypobromous acid and molecular bromine. To avoid undue complications due to a changing ratio of tribromide to bromine during the course of the reaction, the wave length 452 mμ was used for these studies, because the extinction coefficients of tribromide and bromine are equal at this wave length. In these experiments the ratio $(HOBr)/(Br_2)$ was of the order 10^{-4}–10^{-5}, and hypobromous acid did not contribute to the light absorption. It was necessary for the concentration of the reagents to be *ca.* 3×10^{-3} M to give suitable optical densities; the half-times of the reactions were *ca.* 1–1.5 minutes.

The results of one of the runs are displayed in Fig. 1. The plot of log $(Fe^{++})/(\Sigma\ Br_2)$ has a negative second derivative because the bromide ion formed in the course of the reaction increases the tribromide ion concentration, thus accelerating the reaction. The data were analyzed in terms of the assumed rate equation

$$\begin{aligned} -d(\Sigma Br_2)/dt &= (Fe^{+2})[k_2(Br_3^-) + k_5(Br_2) + k_{14}(HOBr)] \quad (13) \\ &= k\,(Fe^{+2})\,(\Sigma Br_2) \end{aligned}$$

The mean constants, k, at a set of times were calculated from the slopes of the plot of log $(Fe^{++})/(\Sigma\ Br_2)$. From these was subtracted $\bar{k}_2 = k_2 \cdot (Br_3^-)/(\Sigma\ Br_2)$, the contribution of tribromide ion to the mean rate constant. For the remaining term

$$\begin{aligned} k - \bar{k}_2 &= \frac{k_5(Br_2) + k_{14}(HOBr)}{\Sigma(Br_2)} \quad (15) \\ &= [k_5 + (k_{14}K_H/(H^+)(Br^-)]/[1 + (Br^-)/K_D) \end{aligned}$$

For K_H,[17] the hydrolysis constant of bromine, we use 1.56×10^{-8} (mole/liter).[2] For the runs at $(H^+) = 0.87$ and 0.50 M, the quantity $k - \bar{k}_2$ was constant within the experimental error of ±10%; for the run at $(H^+) = 0.15$ M, there was a marked decrease in $k - \bar{k}_2$ during the course of the reaction. The results can all be interpreted reasonably well by the values, $k_5 = 0.76$ (liter/mole sec.) and $k_{14} = 2.1 \times 10^4$ (liters/mole sec.)

Table IV displays the data for the course of the reaction at $(H^+) = 0.15$ M. Table V summarizes the runs at higher acidities; for the experiments of Table V, the contribution of hypobromous acid was relatively small, and the calculated decrease in $k - \bar{k}_2$ during the course of any particular reaction was less than 15%.

Table IV

Reaction at Low Bromide, $(H^+) = 0.15$ M, 29.8°, $\mu = 1.0$

t (sec.)	$(\Sigma Br_2) \times 10^3$	log $(Fe^{++})/(\Sigma Br_2)$	$(Br^-) \times 10^3$	k	$k - \bar{k}_2$, obsd.	$k - \bar{k}_2$, calcd.
0	2.50	0.0864	1.02			
19	2.23	.0511	1.56	2.86	2.02	2.10
23	2.16	.0403	1.70	2.86	1.95	1.99
28	2.10	.0302	1.82	2.86	1.88	1.90
33	2.03	.0170	1.96	2.86	1.81	1.81
40	1.95	.000	2.12	2.86	1.73	1.73
47	1.86	− .0214	2.30	2.86	1.63	1.65
56	1.80	− .0376	2.42	2.86	1.57	1.60
65	1.72	− .0625	2.58	2.86	1.49	1.54
83	1.61	− .1029	2.80	2.86	1.38	1.47

Table V

Reactions at Low Bromide, 29.8°, $\mu = 1.0$

$(Fe^{++})_0 \times 10^3$	$(\Sigma Br_2)_0 \times 10^3$	$(Br^-)_0 \times 10^3$	(H^+)	k	$k - \bar{k}_2$, obsd.	$k - \bar{k}_2$, calcd.
3.32	2.73	1.72	0.50	2.19	1.01	1.02
4.15	2.75	2.08	.50	2.32	1.09	1.01
4.15	3.39	2.28	.50	2.45	1.03	0.97
3.32	3.39	1.39	.50	2.35	1.18	1.03
3.05	2.97	1.69	.87	1.87	0.87	0.94

We assume that molecular bromine and hypobromous acid react *via* the reaction paths

$$Fe^{++} + Br_2 \longrightarrow Fe^{+++} + Br_2^-;\ k_5 = 0.76\ (\pm 0.2) \quad (5)$$

$$Fe^{++} + HOBr \longrightarrow FeOH^{++} + Br;\ k_{14} = 2.1\ (\pm 0.4) \times 10^4 \quad (4)$$

Catalysis by Phosphoric Acid.—While developing a procedure for the coulometric titration of dipositive iron with electrolytically generated chlorine or bromine, using an amperometric end-point, Farrington[7] observed that the rate of reaction between halogen and iron(II) was increased by the addition of phosphoric acid. We have made a brief study of this effect. Each run proved to be a good second-order reaction. The reaction rate is decreased as the hydrogen ion concentration is raised. The data, displayed in Table VI, have been analyzed in terms of the rate law

$$-d(\Sigma Br_2)/dt = (Fe^{++})(Br_3^-)[k_2 + k_{17}(H_2PO_4^-)] \quad (16)$$

where $(H_2PO_4^-) = 0.015\ (H_3PO_4)/(H^+)$.[18]

The results in Table VI were not expected to be very precise because the analysis of the experimental data involves subtraction of a substantial contribution to the optical density due to iron(III) phosphate complexes.[11] Apart from the first entry in the table, for which the experimental error is expected to be relatively large, the data are in

---

[17] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932).

[18] The data of R. Griffith and A. McKeown (*Trans. Faraday Soc.*, **36**, 776 (1940)) give for K_1, the first ionization constant of phosphoric acid, $K_1 = 0.016$ at 30°, $\mu = 0.56$ (KCl). O. Lanford and S. Kiehl, (*J. Am. Chem. Soc.*, **64**, 292 (1942)) give $K_1 = 0.030$, at 30°, $\mu = 0.665$ ($NaNO_3$).

TABLE VI

CATALYSIS BY PHOSPHORIC ACID, 29.8°, μ = 1.0

$(Fe^{++})_0$ × 10^5	$(\Sigma Br_2)_0$ × 10^5	(ΣH_3PO_4)	(H^+)	$k_2 + k_{17}$ $(H_2PO_4^-)$	k_{17} × 10^{-3}
Expt. at (Br^-) = 0.5 *M*					
7.42	5.69	0.089	0.516	47.1	5.22
12.54	4.56	.149	.516	43.9	2.35
7.42	5.59	.178	.516	44.9	2.17
7.42	5.56	.267	.516	48.9	1.98
12.54	4.46	.297	.516	46.1	1.44
12.54	4.43	.445	.516	62.4	2.26
7.42	5.62	.446	.516	56.8	1.81
7.42	5.71	.534	.516	70.6	2.42
Expt. at (Br^-) = 0.2 *M*					
6.27	4.71	0.149	0.147	64.3	2.19
6.27	5.42	.149	.300	53.1	2.69
6.27	5.24	.149	.491	47.6	3.07
6.27	5.27	.149	.646	45.5	3.40
6.27	4.85	.446	.344	74.6	2.18
6.49	4.82	.461	.508	70.4	2.75
6.27	5.20	.446	.646	60.2	2.59

moderately satisfactory agreement with the assumed rate law. No other one term expression for the effect of phosphoric acid would satisfy the data as well. (In particular, a rate term, $k(H_3PO_4)(HOBr)(Fe^{++})$, would give correctly the dependence on acidity but not the dependence on bromide ion concentration.) There are indications that k_{17} increases as the hydrogen ion concentration is raised, suggesting that undissociated phosphoric acid is also a catalyst. The results however are not sufficiently accurate to permit reliable conclusions about such finer points.

The reaction mechanism may be formulated as

$$Fe^{++} + Br_3^- + H_2PO_4^- \longrightarrow FeH_2PO_4^{++} + Br^- + Br_2^- \quad (17)$$

It is reported however that the main iron phosphate complex in dilute acid solutions is $FeHPO_4^+$.[19] The absorption spectrum of a 10^{-3} *M* Fe^{++} solution with $(H^+) = 0.5$ *M*, $(H_3PO_4) = 1.5$ *M*, did not show any absorption that could be attributed to a ferrous-phosphoric acid complex.

Acknowledgments.—We are indebted to the Atomic Energy Commission for the support of this research. One of us (P.R.C.) gratefully acknowledges the award of an Allied Chemical and Dye Corporation predoctoral fellowship for the year 1951–1952. Some preliminary investigations of the rate of this reaction were made for us by Mr. James Ibers. We are indebted to Professor Dan H. Campbell for many kindnesses in connection with the use of the Beckman spectrophotometer.

DISCUSSION

N. URI (University of Chicago).—The catalytic decomposition of hydrogen peroxide in the presence of ferric ions follows the rate law, etc.

$$\frac{-dH_2O_2}{dt} = K\,\frac{[Fe^{3+}][H_2O_2]}{[H^+]}$$

This equation holds when hydrogen peroxide is present in excess. When, however, the ferric ion concentration becomes comparable with that of hydrogen peroxide there is considerable deviation in this rate law. I have shown (Uri, *Chem. Reviews*, in press) that the results of Andersen (Andersen, *Acta Chimica Scandinavica*, **2**, 1 (1948)) who carried out a detailed experimental study of this range can be most satisfactorily interpreted if the equation $Fe^{3+}OH^- + OH \rightarrow Fe^{2+} + H_2O_2$ is assigned a significant role. This would be very close to the interpretation presented by Davidson of the inhibition effect caused by ferric ion. The mass spectrographic studies carried out by Cahill and Taube (Cahill and Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952)) favoring a two-electron transfer should not be overlooked and the conflicting evidence should await further clarification.

N. DAVIDSON.—The results reported in our paper show that the reaction path $Fe^{++} + Br_3^- \rightarrow Fe^{+++} + Br^- + Br_2^-$ is preferred to the reaction path $Fe^{++} + Br_3^- \rightarrow Fe^{+4} + 3Br^-$. The reason is presumably that Br_2^- is not a strong enough oxidizing agent to oxidize Fe^{+++} to Fe^{+4}. The potential of the bromide ion, bromine atom couple is −1.9 volts; that of the Br^-, Br_2^- couple perhaps −1.7 volts. Therefore, it is probable that the Fe^{+++}, Fe^{+4}, potential is more negative than −1.7 volts.

A similar investigation of the $Fe^{++} + Cl_2$ reaction is desirable. This would compare the Fe^{+++}, Fe^{+4} couple with the Cl^-, Cl_2^- couple (−2.3 to −2.5 volts). In this connection, I should remind you of the remark by Hochhauser and Taube [I. Hochhauser and H. Taube, *J. Am. Chem. Soc.*, 69, 1582 (1947)] that the comparison of the photochemical and ferrous induced chlorinations of oxalic acid serves to show that chlorine atoms are the chain carriers, but that such studies do not prove whether Fe^{+4} or chlorine atoms are formed in the chain initiating step.

Connick and Awtrey at Berkeley made a brief, preliminary study of the Fe^{++}, Cl_2 reaction, and Dr. Connick has very kindly permitted me to quote their result. In 1 *M* HCl at 25°, assuming $-d(\Sigma Cl_2)/dt = k(Fe^{++})(\Sigma Cl_2)$ (this rate law was confirmed only for the (Fe^{++}) dependence), $k = 55$ liter/mole sec., *i.e.*, about the same as for the Fe^{++}, Br_3^- reaction. Whether the reaction was due to Cl_3^- or Cl_2 has not yet been determined.

The pre-exponential factor for the reaction between Fe^{++} and Br_3^- is $10^{7.6}$ (liter/mole sec.). At zero ionic strength it is probably about $10^{8.6}$. A "normal" bimolecular collision number is 10^{10}, and the positive electrostatic entropy of activation [S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 435] for a reaction between a dispositive and uninegative ion contributes a factor of 10^4, so that a "normal" pre-exponential factor for a reaction of this kind is 10^{14}. The observed factor is 10^{-5} smaller; this negative entropy of activation term is presumably due to a rigid structure for the activated complex, with the corresponding conversion of rotational degrees of freedom into vibrational ones [Ref. 21, p. 19]. We may regard the reaction as an electron transfer reaction (A), or as a bromine atom transfer reaction (B).

	ΔF	ΔH
	kcal.	
(A) $Fe(H_2O)_6^{++} + Br_3^- = Fe(H_2O)_6^{+++} + Br_2^-$	8.8	1.0
(B) $Fe(H_2O)_6^{++} + Br_3^- = Fe(H_2O)_5Br^{++} + H_2O + Br_2^-$	8.0	7.0

The experimental heat of activation is 8.4 kcal. If A is the reaction path, the heat of activation is greater than the heat of reaction because of the Franck–Condon requirement for the configuration of the activated complex. If B is the reaction path, the difference between ΔH and the heat of activation is surprisingly small.

I believe that the reaction between Fe^{++} and H_2O_2 is most reasonably formulated as a hydrogen atom transfer

	ΔF	ΔH
$Fe(H_2O)_6^{++} + H_2O_2 = Fe(H_2O)_5(OH)^{++} + HOH + OH$	+2.0	+2.4

In this case,[2] the rate constant is given by $k = 10^{8.6}$ exp. $(-9400/RT)$. ΔH is again a few kilocalories smaller than the heat of activation.

---

[19] O. E. Lanford and S. J. Kiehl, *J. Am. Chem. Soc.*, **64**, 292 (1942).

THE DISPROPORTIONATION OF MANGANATE ION. MANGANESE DIOXIDE AS HETEROGENEOUS CATALYST

By Frederick R. Duke

Institute for Atomic Research and the Department of Chemistry, Iowa State College, Ames, Iowa

Received March 13, 1952

The disproportionation of manganate by the reaction $3MnO_4^= + 4H^+ \rightleftarrows MnO_2 + 2MnO_4^- + 2H_2O$ has been studied kinetically. A long induction period is followed by a more rapid heterogeneous step in which manganese dioxide, the reaction product plays the role of heterogeneous catalyst. Since the catalysis is specific by MnO_2, the latter probably enters chemically into the reaction through MnO_2 and Mn_2O_3 acting as oxidant and reductant for manganate successively. The induction period is believed to involve pentavalent manganese.

A study of the kinetics of the reaction

$$3MnO_4^= + 4H^+ \rightleftarrows MnO_2 + 2MnO_4^- + 2H_2O$$

was undertaken to learn more about this possibly important step in the reduction of permanganate. Schlesinger and Siems[1] have determined the equilibrium constant for the above reaction and have indicated that the rate of approach to equilibrium is increased by the presence of solid MnO_2.

In order to avoid the task of studying the kinetics of this reaction under conditions of chemical reversibility, tetraphenylarsonium (T.P.A.) ion was added to precipitate the permanganate[2] as it formed; under these conditions the reaction proceeded to completion.

Since the reaction is heterogeneous, there is a long induction period if no MnO_2 is added. Presumably the reaction which occurs during the induction period is homogeneous, leading eventually to the production of MnO_2, after which the reaction becomes heterogeneous and proceeds at a much increased rate.

Experimental

The manganate was prepared by fusing C.P. $KMnO_4$ with four times its weight of C.P. KOH in a platinum crucible and the solidified mixture stored over solid NaOH in a desiccator. The resulting manganate was free from permanganate and was analyzed iodometrically for manganate and the free alkali content determined by titration with standard HCl. Other reagents used were of C.P. grade. All solutions were prepared with conductivity water.

The tetraphenylarsonium chloride used was obtained from the Hach Chemical Co., Ames, Iowa, and was tested for interfering impurities in the following way: An aliquot of volumetrically standardized permanganate solution was added to an excess of the tetraphenylarsonium chloride solution made alkaline with KOH. All of the permanganate was found in the precipitate (calculated 101.6 mg.; found 101.4, 101.8, 102.0 mg.). Then an aliquot of volumetrically standardized manganate solution was allowed to disproportionate completely in 2 *M* alkali with an excess of the tetraphenylarsonium chloride present. The resulting precipitate contained two permanganate ions and one MnO_2 for every three original manganate ions (calculated 77.2 mg., found 77.5 mg.; calculated 128.7 mg., found 128.4 mg.). We therefore concluded that neither the tetraphenylarsonium ion nor any impurity present was oxidizable under the conditions of the experiments.

In the experiments, sufficient manganate to give an extinction at 600 mμ of about 1.0 was added to a 50-ml. volumetric flask. The amount of 1 *M* KOH and NaCl solutions was added to yield the desired alkalinity and ionic strength, and a tenfold excess of tetraphenylarsonium chloride was added. The mixture was diluted to the mark and kept in a constant temperature water-bath maintained at room temperature (27.8 ± 0.1°). Analyses were done by removing a sample, filtering through sintered glass into the cell of a Coleman spectrophotometer followed by a determination of the extinction at 600 mμ.

The freshly precipitated manganese dioxide was prepared by adding methanol to neutral permanganate solution followed by repeated washing on the centrifuge, until washings and a portion of the precipitate gave no change in color upon adding KOH and a drop of permanganate. The aluminum hydroxide was precipitated with ammonia from aluminum chloride solution and thoroughly washed on the centrifuge; ferric hydroxide was prepared similarly.

One experiment was performed without the addition of T.P.A. with the objective of studying the induction period. A manganate solution with an initial absorbency of 0.5 in 0.01 *M* NaOH was placed in a Cenco-Sheard Spectrophotelometer and the absorbencies at 520 mμ (MnO_4^-) and at 600 mμ ($MnO_4^=$) were determined as a function of time. An occasional check of the absorbency at 400 mμ was taken to find the point where MnO_2 began to appear.

Results and Discussion

The data on typical runs are presented in Figs 1 and 2. It is apparent from Fig. 1 that a product of the reaction is a heterogeneous catalyst for the disproportionation. The long induction period which is quite sensitive to *p*H apparently includes a very slow process in which a small amount of the products, manganese dioxide and tetraphenylarsonium permanganate are ultimately formed. The manganese dioxide then catalyzes the reaction and there is a zero order dependency on manganate for most of the reaction. The catalyzed reaction is very nearly second order in hydrogen ion.

Figure 2 demonstrates three phenomena: (1) as the stock solutions ages, a subtle change not readily detectable by optical means occurs which removes the induction period and speeds the process; (2) the MnO_2 is a catalyst and tetraphenylarsonium permanganate, glass wool, and ferric and aluminum hydroxides are not; (3) the manganese dioxide loses its catalytic activity upon aging. Thus, manganese dioxide kept under water for four hours was much less effective than freshly precipitated material.

A possible explanation for these observations may be reached from the mechanism

$$MnO_4^= + MnO_2 \rightleftarrows MnO_2{\cdot}MnO_4^= \quad \text{(adsorption, far to the right)} \qquad (1)$$

$$MnO_2{\cdot}MnO_4^= + 2H^+ \longrightarrow MnO_4^- + Mn\,(III) \text{ in the ppt. (the measured reaction)} \qquad (2)$$

$$2Mn(III)\,(\text{ppt.}) + MnO_4^= \longrightarrow 3MnO_2 \qquad (3)$$

$$MnO_2\,(\text{active}) \longrightarrow MnO_2\,(\text{inactive}) \qquad (4)$$

Reaction (1) explains the zero order in manganate, provided the adsorption is essentially com-

---

[1] H. I. Schlesinger and H. B. Siems, *J. Am. Chem. Soc.*, **46**, 1965 (1924).

[2] H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186 (1939).

plete, making the limiting factor on the rate the amount of active manganese dioxide. If the amount of adsorbed manganate depends upon the surface area of the MnO_2 and the rate of reaction (4) depends upon the total amount of MnO_2 present, a steady state in surface area could be set up, only to break down when insufficient manganate remained to cover the surface of the active MnO_2. The deactivation process for the MnO_2 may be a large change in particle size, or it may be a more subtle change, such as dehydration or some other chemical process. At any rate, freshly precipitated MnO_2 rapidly loses its catalytic activity (Fig. 2).

The lack of catalysis, especially by ferric and aluminum hydroxides, suggests that the manganese dioxide enters into the reaction chemically. Thus, if the precipitate were able to oxidize manganate to permanganate and if the manganate were capable of reoxidizing the reduced manganese in the precipitate, the path indicated by reactions 2 and 3 would be realized. The specific chemical action of precipitated manganese dioxide is also suggested by analogy with the work of Mooi and Selwood,[3] who found magnetic evidence that MnO_2 entered chemically into the heterogeneous decomposition of hydrogen peroxide through a Mn(IV)–Mn(III) path. It appears, then, that the peculiar thermodynamic properties of MnO_2 make this reaction possible in alkaline solution.

The homogeneous reaction during the induction period was also studied. Equilibria of the type: $2MnO_4^{=} \rightleftarrows Mn(V) + MnO_4^-$; and $Mn(V) + MnO_4^{=} \rightleftarrows MnO_2 + MnO_4^-$, both far to the left could be involved in the subtle change which takes place in the manganate solution upon aging. The addition of the precipitant would effectively provide catalytic amounts of MnO_2 through the removal of the permanganate in the above equilibria. The increased rate would then be due to the formation of larger than the steady state amounts of active MnO_2 through displacement of the above equilibria to the right. Mn(V) has been reported[4,5] and its color stated to be blue. In an attempt to find a significant change in the spectrum of the manganate solution upon aging, a series of absorption spectra were made each 24 hours on manganate solutions 1.2 M in $[OH^-]$ having absorbencies of 1 and 2 in 1 mm. cells, using the Carey spectrophotometer. No conclusive differences from day to day were detected, the permanganate spectrum appearing, within observation error, at the same time as the MnO_2 precipitate. Thus the above equilibria must lie far to the left. Another experiment, in which fresh manganate was allowed to disproportionate in the absence of T.P.A., yielded an interesting result pertinent to the induction period. With $[OH^-] = 0.01\ M$, the intermediate blue color of Mn(V) appears to accumulate to a greater extent during the reaction, than is the case at higher alkalinities. Knowing the molar absorbency of both permanganate and manganate at 600 mμ ($MnO_4^{=}$) and 525 mμ (MnO_4^-), it was possible to calculate both of these species as the reaction proceeded by taking absorbency readings at both of these wave lengths. It was found that the permanganate concentration increased from zero to $3.5 \times 10^{-5}\ M$ with a corresponding change in manganate concentration 5×10^{-4} to 4.9×10^{-4}. At the same time, the absorbency at 400 mμ, strongly affected by MnO_2, did not change. It was concluded that the discrepancy was due to the presence of the colored product, Mn(V).

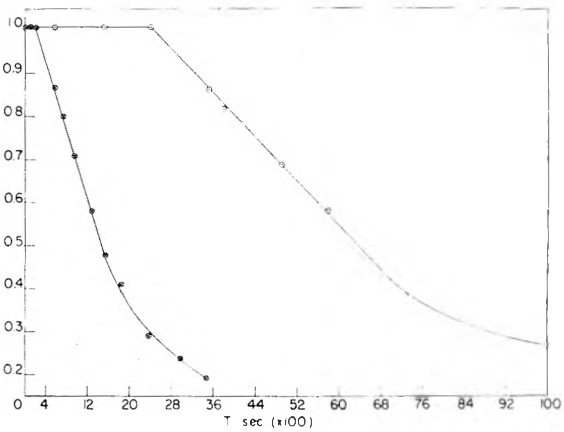


Fig. 1.—⊙, fresh solution of manganate, 0.2 M OH^-, 0.3 M NaCl; ⊗, fresh solution of manganate, 0.1 M OH^-, 0.4 M NaCl.

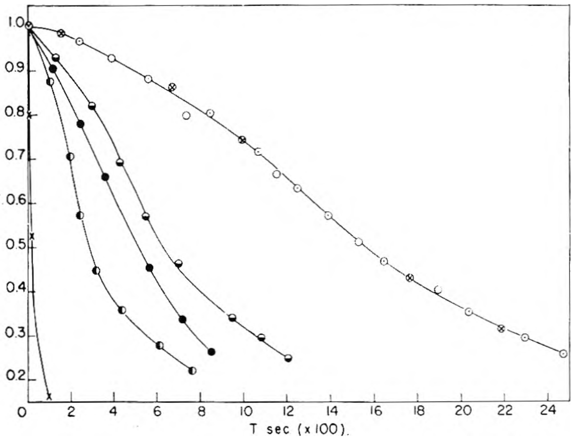


Fig. 2.—○, day old manganate, 0.2 M OH^-, 0.3 M NaCl; ⊗, day old manganate, 0.2 M OH^-, 0.3 M NaCl containing approx. 0.5 g. of $Al(OH)_3$ and 0.5 g. of $Fe(OH)_3$; ⊙, day old manganate, 0.2 M OH^-, 0.3 M NaCl containing approx. 0.5 g. of tetraphenylarsonium permanganate and 0.5 g. of Pyrex wool; ×, day old manganate, 0.2 M OH^-, 0.3 M NaCl containing approx. 0.5 g. of freshly precipitated MnO_2; ●, day old manganate, 0.2 M OH^-, 0.3 M NaCl containing approx. 0.5 g. of MnO_2 kept under water for four hours after precipitating; ◒, three day old manganate, 0.2 M OH^-, 0.3 M NaCl; ◐, week old manganate, 0.2 M OH^-, 0.3 M NaCl.

---

[3] J. Mooi and P. W. Selwood, *J. Am. Chem. Soc.*, **72**, 4333 (1950).

[4] H. Lux, *Z. Naturforsch*, **1**, 281 (1946).

[5] H. H. Miller and L. B. Rogers, *Science*, **109**, 61 (1949).

DISCUSSION

S. E. VOLTZ (Houdry Process Corp.).—Do you consider the lack of catalysis by ferric and aluminum hydroxides as sufficient evidence for assuming that the manganese dioxide enters into the reaction chemically? There are numerous instances in which a reaction is catalyzed by only one particular heterogeneous catalyst. In such cases, the inactivity of a large number of catalysts does not necessarily establish the mechanism by which the active catalyst behaves. Have you considered the possibility of adsorption of the manganate or permanganate ions on the manganese dioxide?

F. R. DUKE. We seldom "really prove" anything in science. However, I consider it an acceptable scientific practice to propose the simplest hypothesis consistent with the facts, so long as we willingly modify the hypothesis to accommodate subsequently discovered facts. I believe that either manganate or permanganate or both may be adsorbed to the manganese dioxide.

R. M. NOYES (Columbia University).—The heterogeneous catalysis might be prevented by using some agent to complex with manganese(V). Previous experiments by H. F. Launer and D. M. Yost, *J. Am. Chem. Soc.*, 56, 2571 (1934), suggest that fluoride ion might prevent the precipitation of manganese dioxide.

DUKE.—This sounds like a very worth while suggestion.

ISOTOPE EXCHANGE REACTIONS OF FLUORINE WITH HALOGEN FLUORIDES

BY RICHARD B. BERNSTEIN[1] AND JOSEPH J. KATZ

Chemistry Division, Argonne National Laboratory, Chicago, Illinois

Received March 18, 1952

The gas phase exchange of radioactive F^{18} between elemental fluorine and the halogen fluorides ClF_3, BrF_5 and IF_7 has been investigated in copper, aluminum and nickel reaction vessels. The rate of isotope exchange at temperatures below 100° was essentially zero in all cases. Complete exchange occurred within a few minutes in the region of 300°, and conveniently measurable rates were observed at intermediate temperatures. To evaluate the heterogeneous contribution to the gas phase exchanges, the behavior of fluorine and the halogen fluorides with AlF_3, CuF_2, NiF_2 and CaF_2 was examined. Fluorine exchange with the metal fluorides was slow; the halogen fluorides exchanged rapidly, but the extent of exchange decreased with increasing temperature. These exchanges are not significant in the temperature range where exchange between fluorine and the halogen fluorides is extensive; consequently the latter exchanges are considered primarily homogeneous. A mechanism for the exchange based on the well-known reversible dissociation of ClF_3 and IF_7 is plausible in the light of the data. Since quantitative data were lacking for IF_7, preliminary measurements of the temperature dependence of the dissociation constant were made, which indicate that the $\Delta H°$ and $\Delta S°$ for dissociation are comparable with the values known for ClF_3. However, in the case of BrF_5, no dissociation was observed up to 400°, and the possibility of an associative mechanism for this exchange is suggested.

Introduction

The radioactive nuclide F^{18} which has a half-life of 112 min. and emits a 0.7 Mev. positron is a convenient tool for the investigation of the behavior of fluorine and its compounds. Dodgen and Libby[2] first employed F^{18} in a study of the exchangeability of fluorine between HF and F_2. Subsequent studies have been made of the fluorine exchange between HF and the halogen fluorides.[3] The two systems were strikingly different. Whereas halogen fluorides were found to exchange very rapidly with HF at room temperature in the gas phase, the corresponding $HF-F_2$ exchange occurred at a negligible rate below 200°. In both cases it was considered necessary to postulate an exchange mechanism which proceeded *via* molecular complex formation. It was thought of interest to extend this work, and the present investigation is concerned with fluorine exchange between gaseous halogen fluorides and elemental fluorine.

Experimental

Materials.—Anhydrous HF and ClF_3 (Harshaw) were purified by distillation. BrF_5 was purified by a vapor phase fluorination to remove BrF_3 (or Br_2) before final distillation. IF_7 was prepared by the fluorination of IF_5 (General Chemical) according to the method of Schumb and Lynch.[4] Fluorine (Pennsylvania Salt) containing approximately 1% inerts was used without further purification. Vapor density determinations of purified IF_7 and ClF_3 samples gave correct molecular weights within 0.5%.

Several methods of incorporating the nuclide F^{18} into the halogen fluoride or fluorine were used. Table I summarizes a number of procedures which have hitherto not been reported. The simplest and most effective procedure so far employed is method 5. In the preparation of labeled elemental fluorine, a high temperature exchange with a labeled halogen fluoride was used. The chemical purification procedures were adequate to ensure no radioactive contamination. In one case the decay of ClF_3^* was observed to decay with the proper half-life over 8 half-lives. In most cases initial specific activities greater than 100 counts/min. per millimole were readily obtained.

TABLE I

PREPARATION OF F^{18} LABELED HALOGEN FLUORIDES

	Material irradiated	Irradiation	Nuclear reaction
1	KHF_2[a]	Betatron (48 Mev. γ)	$F^{19}(\gamma,n)F^{18}$
2	KHF_2[a]	Cyclotron (fast neutrons) $Li^6(d,n)Be^7$	$F^{19}(n,2n)F^{18}$
3	$LiNO_3$[b]	Nuclear reactor	$Li^6(n,\alpha)H^3$ $O^{16}(t,n)F^{18}$
4	$LiAlO_2$[b]	Nuclear reactor	Same as (3)
5	$LiF + Al_2O_3$[c]	Nuclear reactor	Same as (3)

[a] HF^* obtained by pyrolysis of KHF_2^*, and labeled halogen fluoride obtained by gas phase exchange with HF^*. The halogen fluoride* is then purified by treatment with NaF (ref. 3) and subsequent distillation. [b] Treated with liquid hydrogen fluoride to produce HF^* which is purified by absorption on NaF and subsequent pyrolysis of $NaHF_2^*$. Then proceed as in (1). [c] Approximately 1:1 molar ratio of finely powdered and mixed material. Either radioactive halogen fluoride or hydrogen fluoride prepared by direct exchange of liquid with the irradiated solid, followed by distillation.

Apparatus.—A vacuum system similar to that of Rogers and Katz[3] was employed. The apparatus was constructed of copper and nickel throughout with silver-soldered and flared connections. Valves were Crane bellows or Hoke diaphragm type. Fluorethene traps and gages with monel Bourdon tubes were employed; a copper counting vessel into which a Victoreen 1B85 Aluminum Thyrode was sealed served as a suitable counting chamber.[3] The reaction vessels of aluminum and nickel were electrically heated. A Booth–Cromer nickel diaphragm null-type pressure transmitter with an appropriate external pressure balancing system was used when precise pressure measurements were required. A fluorethene weighing ampoule equipped with a special small Crane bellows valve was useful for introducing weighed quantities of halogen fluorides. The pyrolysis chamber for KHF_2 or $NaHF_2$ was constructed of nickel and was surrounded by a furnace.

Method.—A description of an exchange experiment between ClF_3 and F_2 will be given as a typical example of the method employed. A sample of $LiF-Al_2O_3$, after irradiation in the nuclear pile for 1–2 hr., is introduced into a fluorethene trap and evacuated. Approximately one or two ml. of liquid ClF_3 obtained from the center third of a single-plate trap-to-trap distillation is frozen onto the $LiF-Al_2O_3$ mixture, and allowed to warm up to room temperature under its own vapor pressure. The solid–liquid isotope exchange is complete in about 15 min. The ClF_3^* is then purified by further distillation, and the final sample expanded into the counting vessel. Here the specific activity is determined over a period of approximately one quarter-life. The ClF_3^* is transferred into the reaction vessel at its operating temperature. A suitable quantity of fluorine is then introduced and the exchange is allowed to proceed with the vessel cut off from the vacuum line. After the $F_2-ClF_3^*$ exchange has proceeded for the desired

---

[1] Department of Chemistry, Illinois Institute of Technology. Work performed under Participating Institution Program.

[2] H. W. Dodgen and W. F. Libby, *J. Chem. Phys.*, **17**, 951 (1949).

[3] M. T. Rogers and J. J. Katz, *J. Am. Chem. Soc.*, **74**, 1375 (1952).

[4] W. C. Schumb and M. A. Lynch, *Ind. Eng. Chem.*, **42**, 1383 (1950).

Table II

Exchange of Fluorine with Halogen Fluorides

Halogen fluoride	Reaction vessel	Partial pressures (mm.) F_2	Partial pressures (mm.) Halogen fluoride	T, °C.	Contact time, min.	Exchanged, %	Exchange rate r (min.$^{-1}$)
ClF_3	Cu	160	45	25	10	< 2.0	$<2 \times 10^{-3}$
	Cu	85	140	25	40	< 1.0	$< 2 \times 10^{-4}$
	Cu	360	100	25	45	< 0.5	$<10^{-4}$
	Al	500	710	119	45	6.0	1.2×10^{-3}
	Al	360	450	165	40	72.0	3.2×10^{-2}
	Ni	795	120	170	40	12.0	3.2×10^{-3}
	Al	360	590	232	30	95.0	$>10^{-1}$
BrF_5	Cu	150	10	25	30	< 2.0	$<10^{-3}$
	Ni	444	101	181	23	11.0	5.0×10^{-3}
	Ni	532	145	242	18	71.0	6.9×10^{-2}
	Ni	818	237	300	30	91.0	8.0×10^{-2}
	Ni	485	105	300	40	>98.0	$>10^{-1}$
IF_7	Al	665	450	25	25	< 2.0	$<2 \times 10^{-3}$
	Al	845	455	160	40	36.0	1.1×10^{-2}
	Ni	740	200	306	25	95.0	$>10^{-1}$

time, the mixture is passed slowly through two traps in series maintained at −195° to remove the ClF_3*; the F_2* is expanded into the counter. The measured activity of the F_2* is corrected by a PV/T factor to give the total activity of F_2* present in the reaction vessel. Then the fluorine is removed and the total ClF_3* introduced into the counter. The recovery of halogen fluoride is usually greater than 98%. The activity is then measured and the per cent. loss in specific activity due to exchange with F_2 is measured. Due to the exchange with the fluoride coating of the reaction vessel the total inventory of F^{18} was never 100%. Depending on the temperature and the surface the loss due to exchange with the surface would range from 0–30% of the original activity. The gas phase exchange was calculated using the *recoverable* total activity, *i.e.*, the sum of the F_2* and ClF_3* activities after exchange.

The loss of F^{18} inventory was shown to be due primarily to exchange with the metal fluoride coating by experiments using subsequent elution with tank ClF_3. This elution could not be accomplished, however, by elemental fluorine in a reasonable time. The "fraction exchanged" was calculated by dividing the observed percentage of the total activity in the F_2* by the atomic percentage of fluorine in the form of elemental fluorine in the mixture.

Due to the many different conditions under which the various experiments were carried out it is difficult to state an over-all probable error. One of the more serious errors may be the excess residual background in the counting chamber due to exchange with the labeled halogen fluoride, for which correction is necessary. By careful attention to detail a satisfactory F^{18} inventory can be obtained. Under the most favorable circumstances it appears that there is an uncertainty in the percentage exchanged of ± 3% exchanged.

Results and Discussion

The experiments carried out in the gas phase between fluorine and the halogen fluorides are summarized in Table II. In addition to the experimental variables, the calculated exchange rate is given, defined $r = -(1/t) \ln(1 - f)$ min.$^{-1}$, where f is the fraction exchanged in a contact time of t minutes. In some cases this must be taken as a lower or an upper limit on the rate for obvious reasons. The few data which lend themselves to calculation of temperature coefficients are those where the percentage exchanged lies between 10 and 90%. With the exception of one experiment with ClF_3 in a nickel reactor the data show qualitative consistency.

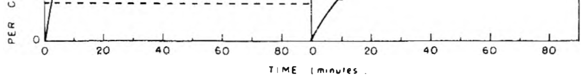


Fig. 1.—Exchange of ClF_3* with CaF_2: - - - - -, calculated loss in activity based on single layer surface exchange; ○, ClF_3 vapor; ◓, ClF_3 liquid.

The rate of isotope exchange between fluorine and the halogen fluorides is seen to be essentially zero at room temperature. Exchange rates in the measureable range occur at elevated temperatures. All of the exchanges proceed to equilibrium in periods of the order of minutes at temperatures in the region of 300°.

Exchange studies to determine the heterogeneous contribution were carried out between each of the halogen fluorides and various solid fluorides including AlF_3, NiF_2, CuF_2 and CaF_2. A number of exchanges were carried out with elemental fluorine and solid fluorides. Figure 1A shows the exchange at room temperature of ClF_3* (liquid) with CaF_2. Figure 1B gives comparable data for ClF_3* (vapor) with CaF_2; in this case after 80 min. the ClF_3* was condensed on the solid and the exchange allowed to continue with liquid ClF_3*. The dotted lines in the diagrams represent the calculated loss in activity of the ClF_3* based upon the assumption of exchange with a single layer of fluoride ions on the crystal. This calculation was made using the known quantities of reactants, the surface area of the powder in cm.^{2}/g. as determined by the B.E.T. nitrogen adsorption method, and the assumed effective area of a single fluoride ion on the surface, $(M/aN_0\rho)^{2/3}$, where M is the molecular weight, a = number of F atoms per molecule, N_0 is Avogadro's number, and ρ the crystal density. In view of the results, it is clear that F^{18} exchange would be difficult to apply to determination of surface area of solid fluorides.

It is seen from Fig. 1 that the extent of exchange is greater in the case of the liquid–solid system than in the vapor–solid system, as might be anticipated on the basis of the probable solubility of the salt in the halogen fluoride with resulting ionic exchange. Similar results were obtained with AlF_3.

The exchange of BrF_5^* with the NiF_2 coating of one of the reactors was carried out at several temperatures. Table III lists the results, including one comparable measurement with ClF_3^*.

TABLE III

EXCHANGE OF BrF_5^* AND ClF_3^* WITH NiF_2

Halogen fluoride	T, °C.	Time, min.	Pressure, mm.	Loss in activity, %	No. of gram atoms of F on surface which exchanged
ClF_3^*	25	42	149	6.8	3.8×10^{-3}
BrF_5^*	26	56	94	7.4	4.4×10^{-3}
BrF_5^*	253	38	141	4.7	2.3×10^{-3}
BrF_5^*	321	33	130	2.0	0.8×10^{-3}

Thus it appears that an increase in temperature reduced the extent of exchange in the vapor–solid system. This is reasonable on the basis of a surface film of adsorbed halogen fluoride in which ionic exchange with the solid fluoride may occur. Increasing the temperature would reduce the adsorption and thus the exchange.

It is of particular importance that elemental fluorine was found to exchange with various solid (labeled) fluorides at a small fraction of the rate of the halogen fluoride-metal fluoride exchanges. This fact, together with the negative temperature coefficient of the surface exchange of the halogen fluorides, would indicate that the observed isotope exchanges between fluorine and the halogen fluorides reported in Table II are primarily homogeneous. The mechanism which suggests itself for the homogeneous exchange involves the reversible dissociation of the halogen fluoride to a lower fluoride and fluorine. Equilibrium constants for the reaction $ClF_3 = ClF + F_2$ as a function of temperature are known.[5] Such a dissociation would provide a suitable path for the exchange. A similar dissociation of IF_7 to IF_5 and BrF_5 to BrF_3 and fluorine would *a priori* seem reasonable. Consequently, the thermal stability of IF_7 and BrF_5 were examined.

Dissociation equilibrium constants for IF_7 and BrF_5 were measured and compared with known data for ClF_3. The measurements were carried out in a two-liter nickel vessel of accurately known volume. The degree of dissociation was determined by observing the deviation from ideal gas behavior. The apparatus was checked with He and ClF_3 before use with IF_7 and BrF_5. The preliminary measurements on IF_7 are shown in Fig. 2 in which the log K_p (atm.) is plotted *vs.* $1/T$. The points at low temperatures are quite uncertain and have been given little consideration. From these data the values of $\Delta H°$ and $\Delta S°$ are 28.5 ± 2.0 kcal./mole and 43.5 ± 3.0 e.u., respectively. Further measurements of higher precision are in progress.

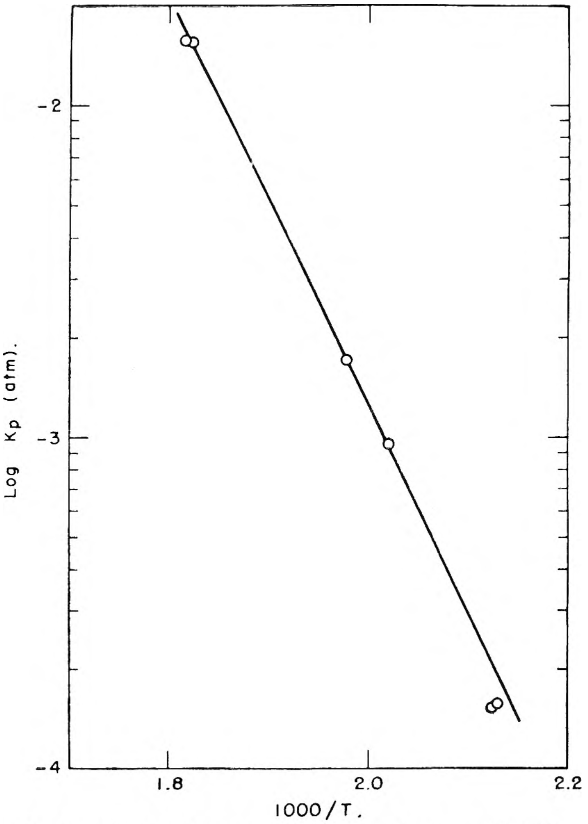


Fig. 2.—Dissociation equilibrium constant *vs.* 1000/T.

$$IF_7 = IF_5 + F_2 \begin{cases} \Delta H° = 28.5 \pm 2.0 \text{ kcal./mole} \\ \Delta S° = 43.5 \pm 3.0 \text{ e.u.} \end{cases}$$

It is seen that these values are quite comparable with those for ClF_3, *i.e.*, $\Delta H° = 25$ kcal./mole, $\Delta S° = 32$ e.u. In both cases sufficient dissociation occurs in the temperature range 100–300° to account for the observed isotopic exchange rates on the basis of a dissociative mechanism.

In the case of BrF_5, however, measurements up to 400° revealed less than 0.1% dissociation (the limit of precision of the apparatus), corresponding to a value of $\Delta F° > 18$ kcal./mole at 670° K. Assuming a reasonable value for the $\Delta S°$ of the dissociation (35 e.u.), this result implies that $\Delta H°$ must be greater than 42 kcal./mole. The thermal stability of BrF_5 has been noted previously by Ruff and Menzel.[6]

Since the dissociative mechanism appeared unlikely in the case of BrF_5, several experiments were performed with the aim of detecting possible association or complex formation between BrF_5 and F_2. With an equimolar mixture it was found that negative pressure deviations of the order of 1–2% occurred at temperatures above 250°. Although the interactions which are manifested in this way are probably sufficient to account for the isotope exchange between BrF_5 and F_2, the data are not definitive evidence for complex or compound formation in the usual sense since no net loss in pressure was found upon cooling the mixture to room temperature. A complex more stable at the elevated temperatures seems somewhat unlikely. This point requires further experimental investigation before a satisfactory interpretation may be offered.

In the case of the fluorine exchanges with ClF_3

---

[5] (a) H. Schmitz and H. Schumacher, *Naturforsch.*, **2A**, 362 (1947); (b) K. Schäfer and E. Wicke, *Z. Elektrochem.*, **52**, 205 (1948).

[6] O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **202**, 49 (1931).

and IF_7 it would seem possible to test directly the assumption of the dissociative mechanism in a more quantitative fashion with more precise kinetic data. If we assume that the rate-limiting step in the isotope exchange is the dissociation

$$XF_n \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} XF_{n-2} + F_2$$

with $k_1/k_{-1} = K_p$, we have

$$XF_{n-1}F^* \rightleftarrows XF_{n-2} + FF^* \qquad (1)$$

and

$$F_2 + XF_{n-2} \rightleftarrows XF_n \qquad (2)$$

For $K_p \ll 1$, assuming the rate-determining step in the mechanism is (1), then

$$R = k_1[XF_n]$$

where R is the rate of dissociation of the halogen fluoride and $[XF_n]$ is its partial pressure (atm.). For the isotopic exchange reaction, (1) + (2)

$$XF_{n-1}F^* + F_2 \rightleftarrows XF_n + FF^*$$

we may use the method of McKay[7] to calculate the rate of appearance of activity in the fluorine. Letting

$$[XF_n] = a,\ [F_2] = b$$

and

$$[XF_{n-1}F^*] = xa,\ [FF^*] = yb$$

then

$$\frac{d}{dt}(yb) = R\left[\frac{x}{n} - \frac{y}{2}\right]$$

but

$$xa + yb = x_\infty a + y_\infty b$$

and

$$x_\infty = \frac{n}{2}y_\infty$$

so we have the result

$$\frac{dy}{dt} = R\left(\frac{na + 2b}{2nab}\right)(y_\infty - y)$$

$$\text{or } r \equiv -\frac{d\ln(1-f)}{dt} = R\left(\frac{na + 2b}{2nab}\right)$$

where f = fraction exchanged. Substituting for R we have

$$r = -\frac{d\ln(1-f)}{dt} = k_1\left[\frac{1}{n} + \frac{[XF_n]}{2[F_2]}\right]$$

Thus a plot of the quantity $-(1/t)\ln(1 - f)$, *vs.* the molar ratio of halogen fluoride to fluorine should be linear, with an intercept k_1/n. For a reaction proceeding by such a mechanism, the value of the dissociation rate constant k_1 may thus be obtained at temperatures considerably below those at which direct kinetic measurements of the rates of dissociation of slightly dissociated compounds are possible. This procedure may possibly have some general applicability in determination of rates of dissociation.

Acknowledgments.—The authors appreciate the help of Mr. Richard M. Adams who assisted in obtaining the data in the latter phases of this work. The authors appreciate the coöperation of Mr. W. H. McCorkle and the operators of the nuclear reactor at the Argonne National Laboratory. Thanks are also due to Mr. C. McKinney and the operators of the betatron at the University of Chicago, and to Mr. M. Fielding of the small cyclotron of the University of Chicago.

---

[7] H. A. C. McKay, *Nature*, **142**, 997 (1938).

THE SIGNIFICANCE OF ISOTOPIC REACTIONS IN RATE THEORY

BY HENRY EYRING AND F. WM. CAGLE, JR.
Department of Chemistry, University of Utah, Salt Lake City 1, Utah

Received March 6, 1952

The general theory of the isotopic effect on reaction rates is developed in terms of the absolute rate theory. The high temperature limit of the separation factor $(m^{\ddagger}_{\text{heavy}}/m^{\ddagger}_{\text{light}})^{1/2}$ is obtained and its significance and use discussed. The possibility of obtaining an α of less than unity is investigated and the rather physically unlikely conditions which would be necessary are stated. The electrolytic concentration of heavy water is considered since it provides a reaction with at least two mechanisms. An approximate separation factor is discussed for one mechanism and the unusual increase of separation factor with temperature, over a limited temperature range, is discussed. A very tentative activated complex is postulated for the hydrolysis of Al_4C_3 which explains the unusually high separation factor (*ca.* 20) for the reaction with H_2O compared with D_2O. Four organic reactions involving isotopes for which separation factors have been observed are considered in light of a simplified model. Very good agreement between calculated and observed separation factors is obtained.

Theory of Isotopic Separation Coefficients.—The general principles in isotopic reactions are well understood.[1-10] If we can guess what the activated complex is and if we know the normal state of our system, we can write, in terms of partition functions, the ratio α of the specific rates for the light over the heavy isotopic reaction. Since the potential surfaces in configuration space are the same for all isotopes, we can use the same classical activation energy, E_c, for all reactions (see Fig. 1). In this case, the partition functions for vibrational degrees of freedom f_v can be written $f_v = [2 \sinh (h\nu/2kT)]^{-1}$. The other types of degrees of freedom have the usual forms with the usual meanings for the symbols. Thus

$${}_{2\mathrm{R}} = \frac{8\pi^2 IkT}{\sigma h^2}, f_{3\mathrm{R}} = \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}$$

$$\text{and } F_{3\mathrm{T}} = \frac{(2\pi mkT)^{3/2}}{h^3}$$

Here f_{2r}, f_{3r} and F_{3t} refer to two and to three rotational degrees of freedom and to three translational degrees of freedom per unit volume, respectively. We use the symbol $\ddagger$ to indicate the activated state. Thus, k' for any gaseous reaction involving a linear activated complex is[11]

$$k' = \frac{\kappa kT}{h} \frac{F^{\ddagger}_{3\mathrm{T}} f^{\ddagger}_{2\mathrm{R}} \overset{g}{\underset{j=1}{\pi}} [2 \sinh(h\nu_j^{\ddagger}/2kT)]^{-1}}{F_i} \exp(-E_c/RT) \qquad (I)$$

Here F_i is the appropriate product of partition functions for the degrees of freedom in the initial state. If the activated complex is non-linear f_{3r} replaces f_{2r} and one vibration. It will be remembered that one of the degrees of freedom of the activated complex is included in the factor kT/h. Barrier leakage is negligible unless one is considering a small class of reactions including, for example, the inversion of ammonia. In condensed phases, degrees of freedom which in the gas are translations and rotations are sometimes better represented as vibrations. The separation factor

$$\alpha \equiv k' \text{ light isotope}/k' \text{ heavy isotope} \qquad (II)$$

thus can be uniquely calculated whenever we know the mechanism and the potential surface involved. The factor $\exp(-E_c/kT)$ appearing in numerator and denominator of α disappears as do those partition functions for degrees of freedom not involving the isotopes. Because part of the separation factor is due to quantum effects α approaches $\alpha_{\text{limit}} = (m^{\ddagger}_{\text{heavy}}/m^{\ddagger}_{\text{light}})^{1/2}$ at high temperatures for all mechanisms. Here both the $m^{\ddagger}$'s in α_{limit} refer to the reduced mass along the reaction coördinate. In a diffusion mechanism, these reduced masses are just the masses of the diffusing molecules. In other cases α_{limit} gives some very interesting information about the nature of the reaction coördinate. By yielding the ratio of reduced masses for light and heavy isotopes along the reaction coördinate, it is indicative of the type of mechanism. The only way to get an α less than unity is to be in the comparatively low temperature region of quantum effects and have the sum of the half quanta for the activated complex exceed the sum for the normal state. If this phenomenon ever occurs, it is excessively rare. When α actually increases with temperature, as it sometimes does, we know this must arise by the reaction shifting with temperature rise from a mechanism with a low α to another mechanism with a higher α Even in this case, as the temperature rises high enough, α must approach $(m^{\ddagger}_{\text{heavy}}/m^{\ddagger}_{\text{light}})^{1/2}$ which is the ratio of velocities along the reaction coördinate,

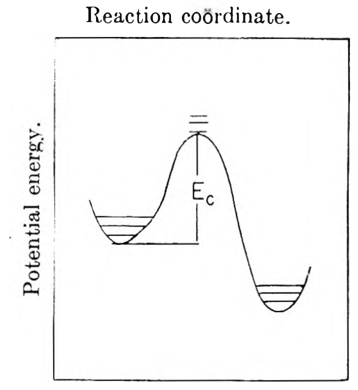


Fig. 1.—Potential energy barrier.

---

[1] R. P. Bell and J. H. Wolfenden, *Nature*, **133**, 25 (1934).

[2] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[3] J. Bigeleisen and M. G. Mayer, *ibid.*, **15**, 261 (1947).

[4] A. J. Edwards, H. F. Walton, R. P. Bell and J. H. Wolfenden, *J. Chem. Soc.* 286 (1936).

[5] H. Eyring, *Proc. Nat. Acad.*, **19**, 78 (1933).

[6] H. Eyring and M. Polanyi, *Z. physik. Chem.*, [B] **12**, 279 (1931).

[7] H. Eyring and A. Sherman, *J. Chem. Phys.*, **1**, 345 (1933).

[8] M. Polanyi, *Nature*, **133**, 26 (1934).

[9] B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934).

[10] H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

[11] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

all contributions of the partition functions to the rates having cancelled out.

Electrode Reactions.—Historically this separation is interesting because it was used to separate deuterium from hydrogen.[12,13] The separation factors indicate electrolysis proceeds by a variety of mechanisms. In an acid or alkaline solution where water is disappearing, the source of the hydrogen or deuterium electrolyzed off is the water rather than the acid or base. Thus water must be used as the initial state in the absolute rate calculation. If one considers a solution of H_2O and DHO and assumes the Erdey–Grúz and Volmer mechanism

$$\mathrm{HOH} + \mathrm{Me} \longrightarrow \mathrm{HO}\text{---}\mathrm{H}\text{--}\mathrm{Me} \longrightarrow \mathrm{HO} + \mathrm{HMe} \quad (1)$$

$$\mathrm{DOH} + \mathrm{Me} \longrightarrow \mathrm{DO}\text{---}\mathrm{H}\text{--}\mathrm{Me} \longrightarrow \mathrm{DO} + \mathrm{HMe} \quad (2)$$

$$\mathrm{HOD} + \mathrm{Me} \longrightarrow \mathrm{HO}\text{---}\mathrm{D}\text{--}\mathrm{Me} \longrightarrow \mathrm{HO} + \mathrm{DMe} \quad (3)$$

The specific rate constant of (1), because of a symmetry factor, is twice the value of (2) and of (3) aside from differences due to zero point energy. Thus, we will write for it the specific rate constant, $2k_1$. Then

$$\frac{\mathrm{d(H)}}{\mathrm{d(D)}} = \frac{2k_1(\mathrm{H_2O}) + k_2(\mathrm{DHO})}{k_3(\mathrm{DHO})} \quad \mathrm{(III)}$$

In fairly good approximation $k_1 = k_2$ so that

$$\frac{\mathrm{d(H)}}{\mathrm{d(D)}} = \frac{k_1[\mathrm{H}]}{k_3[\mathrm{D}]} \quad \mathrm{(IV)}$$

or

$$\frac{\mathrm{d}\ln[\mathrm{H}]}{\mathrm{d}\ln[\mathrm{D}]} = \alpha \equiv \frac{k_1}{k_3} \simeq \frac{\sinh(h\nu_{\mathrm{OH}}/2kT)}{\sinh(h\nu_{\mathrm{OD}}/2kT)} \quad \mathrm{(V)}$$

Here the square brackets indicate concentration of the atom in the water solution. In (V) we have neglected a great deal. In particular, we have assumed the partition function of all degrees of freedom, except for the reaction coördinate, cancel out of α. Further, the partition function for the reaction coördinate in the activated state is absorbed in kT/h and makes no contribution. Finally, we have chosen the reaction coördinate to be the bond involving the dissociating hydrogen isotope. Taking $T = 298°\mathrm{K}$. and $\bar{\nu}_{\mathrm{O-H}} = 3652$ cm.$^{-1}$ and $\bar{\nu}_{\mathrm{O-D}} = 2666$ cm.$^{-1}$ we obtain $\alpha = 10.8$. Experimentally, one observes[9,10] values around $\alpha = 6$ to 7 for metals like Ag, Ni, Pt, Au, Cu and Pb (in alkali) with $\mathrm{d}\alpha/\mathrm{d}T$ negative, while for Hg, Sn and Pb (in acid) $\alpha = 3$ with $\mathrm{d}\alpha/\mathrm{d}T$ small or positive for Hg and Sn. First we see that at least two mechanisms must be involved in electrolysis. A lower α than that calculated would be obtained for any process in which the reaction coördinate involves motion other than a simple pulling away of the hydrogen isotope. The value calculated is thus essentially an upper limit. The low values could come from some such mechanism as a water molecule going across and adsorbing on the cathode, with the slow process, the desorption of an OH^- ion. There are, of course, a variety of other possibilities. The natural thing for a single mechanism is for $\mathrm{d}\alpha/\mathrm{d}T$ to be negative. When it is positive, one can be sure the mechanism shifts from a process with a low α to one with high α with rising temperature.

Some Other Isotopic Reactions.—Aluminum carbide, reacting with H_2O and D_2O[14] to give methane and hydrated aluminum oxide, gives an α near 20. In looking back at our calculation for electrolysis of heavy water, we see that when there was one less bond involving a hydrogen isotope in the activated as compared to the initial state, the separation coefficient α was about 10. An additional factor of 2 in α would mean a decrease of more than one bond involving hydrogen isotopes in the activated state. Thus, if the activated complex were composed of something like an H_2 molecule plus an H^+ ion approaching an adsorbed hydrogen atom we would have but two bonds involving hydrogen atoms, whereas in the ground state, these four atoms were all tied to oxygens. Thus, four bonds in the ground state drop to something around two in the activated state. If one notes that the zero point energy of H_2 is 6.2 kcal. while for OH it is 5.2 kcal., the resulting α is not far from what would be expected from such a mechanism. This example emphasizes that in estimating a separation factor, one should calculate the total difference between zero point energies in the normal and activated state and use this in a Boltzmann expression. The exact calculation, using hyperbolic sines, only changes the result a little at room temperature. α is, thus, a useful tool in proving mechanism.

Some chemical decompositions involving isotopes apparently proceed by the breaking of a bond connected with the isotope. Certain decompositions of this sort have been examined by Bigeleisen[15–20] and by Pitzer.[21] For these reactions the expression for the separation coefficient analogous to (V) is approximately

$$\alpha \equiv k_1'/k_2' \simeq \sinh(h\nu_1/2kT)[\sinh(h\nu_2/2kT)]^{-1} \quad \mathrm{(VI)}$$

In this equation ν_1 and ν_2 represent the frequencies of the hypothetical diatomic molecules of the isotope and the other atom involved in the bond to be broken. That other bonds contribute little to such a reaction has been emphasized by Slater.[22] In general this frequency is known from spectroscopy for the common isotope and can be calculated for the other isotope from the relation of the reduced masses when the value isn't experimentally available.

A particular case of such a decomposition involves the dehydration of formic acid with sulfuric acid. This reaction, producing carbon monoxide, has been studied by Ropp, Weinberger and Neville[23] for formic acid containing C^{14} and C^{12}. The dehydration of the C^{12}-formic acid proceeds more

---

[12] G. N. Lewis, *J. Am. Chem. Soc.*, **55**, 1297 (1934).

[13] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932).

[14] H. C. Urey and D. Price, *J. Chem. Phys.*, **2**, 300 (1934).

[15] J. Bigeleisen, *ibid.*, **17**, 344 (1949).

[16] J. Bigeleisen, *ibid.*, **17**, 425 (1949).

[17] J. Bigeleisen, and T. L. Allen, *ibid.*, **19**, 760 (1951).

[18] J. Bigeleisen, and L. Friedman, *ibid.*, **17**, 998 (1949).

[19] A. A. Bothner-By and J. Bigeleisen, *ibid.*, **19**, 755 (1951).

[20] L. Friedman and J. Bigeleisen, *ibid.*, **18**, 1325 (1950).

[21] K. S. Pitzer, *ibid.*, **17**, 1341 (1949).

[22] N. B. Slater, *Proc. Roy. Soc. (London)*, **A194**, 112 (1948).

[23] G. A. Ropp, A. J. Weinberg and O. K. Neville, *J. Am. Chem. Soc.*, **73**, 5573 (1951)

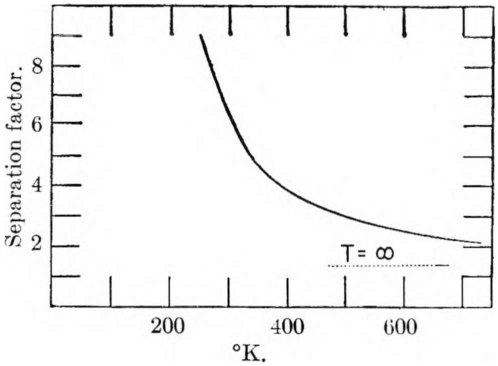


Fig. 2.—Separation factor *versus* temperature for breaking of C^{12}–H *versus* C^{12}–D.

rapidly and this reaction is 11.11% faster at 273°K. and 8.59% faster at 298°K.

Assuming the rate-determining step is breaking the C–O bond, we may calculate the expected separation factor. The wave number for the C^{12}–O^{16} bond is given by Hofstadter[24] to be 1093 cm.$^{-1}$. From this, one calculates for the C^{14}–O^{16} bond the value 1047 cm.$^{-1}$. The calculated values of the separation factors indicate that the C^{12}-formic acid should dehydrate more rapidly than C^{14}-formic acid by 12.8% as compared with 11.11% at 273°K. and 11.5% as compared with 8.59% at 298°K.

Another isotope effect which has received experimental attention is the oxidation of carboxyl-C^{14}-acetic acid. Evans and Huston[25] have determined that this oxidation proceeds more slowly with the C^{14}-acid than with the usual C^{12}-acid. If we assume the rate-determining step is the oxidation in one case of a C^{12}–C^{14} bond and in the other of a C^{12}–C^{12} bond, we may calculate the expected α. The value of $\bar{\nu}$ for the C^{12}–C^{12} bond in acetic acid may be taken to be about 993 cm.$^{-1}$,[26] One then calculates for C^{14}–C^{12} a value of 957 cm.$^{-1}$. From these data one may calculate α at 373°K. to be 1.075. The approximate measured value is 1.05.

Dibeler and Bernstein[27] have studied the isotope effect on the dissociation of CCl_3H and CCl_3D. They find that at 518°K., in the mass spectroscope, the C–H bond in CCl_3H dissociates with a probability of 3.0 times that of the C–D bond in CCl_3D. They compare this value with the similar value of 2.6 for the probability of breaking a C–H bond to a C–D bond in CH_3D given by Boersch.[28] In view of the frequencies of the respective bonds, the separation factor at the same temperatures should be practically identical. If we take the values $\bar{\nu}_{C^{12}-H}$ (3019 cm.$^{-1}$) and $\bar{\nu}_{C^{12}-D}$ (2256 cm.$^{-1}$) given by Wood and Rank[29] for chloroform and deuterochloroform, we calculate at 518°K. a separation factor of 2.89.

Acknowledgment.—We wish to thank the Office of Air Research for support received during this research.

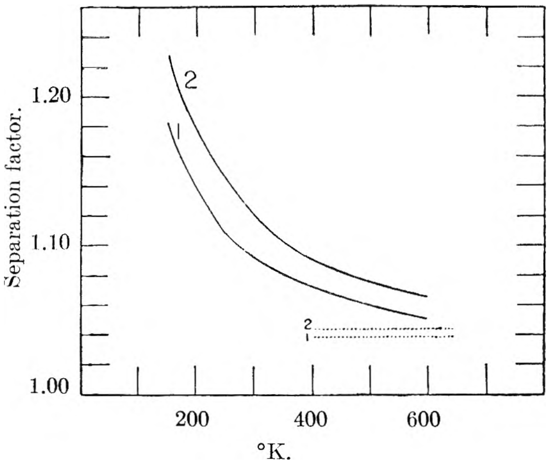


Fig. 3.—1, Separation factor *versus* temperature for breaking of C^{12}–C^{12} *versus* C^{14}–C^{12}; 2, separation factor *versus* temperature for breaking of C^{12}–O^{16} *versus* C^{14}–O^{16}.

DISCUSSION

R. B. BERNSTEIN (Illinois Inst. Tech.).—(1) Ropp, *et al.* (ref. 23 above) express their data in the form $\ln k_{14}/k_{12} = \ln A_{14}/A_{12} - \Delta E/RT$, and state a value of $\Delta E = 189$ cal./mole. Using this value one computes the ratio A_{14}/A_{12} from their data to be 1.25, whereas it would appear more reasonable that this ratio should be less than or equal to unity. If one assumes a limiting upper limit of $A_{14}/A_{12} = 1.00$, the required value of ΔE to fit the data is appreciably smaller than the reported one. This discrepancy is also illustrated by the considerably smaller temperature coefficient for the relative rate as calculated by Eyring and Cagle compared to the data of Ropp, *et al.* No explanation for this difficulty is yet apparent.

(2) It might be of interest to note that if, instead of the observed C–H and C–D stretching frequencies for CCl_3H and CCl_3D, one uses frequencies calculated for the imaginary diatomic molecules C–H and C–D whose force constants are those of the normal molecule (*i.e.*, the concept of Slater, ref. 22, for cases involving the rupture of an isolated bond), the resulting separation factor becomes 2.97. This is, perhaps fortuitously, in better agreement with the data.

J. BIGELEISEN (Brookhaven Nat. Lab.).—I have come to a similar conclusion to the one mentioned by Professor Bernstein with regard to the temperature coefficient of the data of Ropp, Neville and Weinberger. I believe that the difficulty resides in an overestimate on the part of the authors of the precision in their determination of the difference in activation energies.

It might appear to the casual reader that there is a difference between the mathematical expressions for the ratio of rate constants of isotopic molecules used in the present paper and the ones developed and used by me in recent years. It can be shown that for the model used by Eyring and Cagle, the two expressions are mathematical identities. For any other model, there will be differences. The equations which I have used are based on the transition state theory, but are not restricted to any particular model.

G. M. HARRIS (University of Wisconsin).—We have recently been investigating the bromination of methane and monodeuteromethane in an effort to determine the relative rates of chemical reaction at C–H bonds in CH_4, C–H bonds in CH_3D, and C–D bonds in CH_3D. The possible reactions are

$$CH_3D \xrightarrow{3k_1} CH_2DBr$$
$$\xrightarrow{k_2} CH_3Br\text{, and}$$
$$CH_4 \xrightarrow{4k_3} CH_3Br$$

---

[24] R. Hofstadter, *J. Chem. Phys.*, **6**, 540 (1938).

[25] E. A. Evans and J. L. Huston, *ibid.*, **19**, 1214 (1951).

[26] R. B. Barnes, R. C. Gore, U. Liddell and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York N. Y., 1944.

[27] V. H. Dibeler and R. B. Bernstein, *J. Chem. Phys.*, **19**, 404 (1951).

[28] H. Boersch, *Monatsh.*, **66**, 311 (1935).

[29] R. W. Wood and D. H. Rank, *Phys. Rev.*, **48**, 63 (1935).

Our preliminary results indicate $k_1:k_2:k_3$ = 1.17:0.60:1.00, the ratio of the products being obtained by mass spectrometry. Could Professor Eyring suggest a theoretical explanation of the apparent non-identity of k_1 and k_3?

H. EYRING.—A difference of 17% between k_1 and k_3 could arise from so many sources that I would hesitate to suggest more than where to look, without more knowledge of the experimental details. Because of the stiffness of vibration the difference in mass between D and H will be of little effect on stretching vibrations, whereas in bending vibrations it will matter more and it will have its classical effect on rotational degrees of freedom and on the velocity along the reaction coördinate. If the mechanisms are well enough known, even the approximate potential surfaces of the type calculated in "The Theory of Rate Processes" for the activated complex should reveal differences of the observed magnitude.

ENRICHMENT OF ISOTOPES BY DIFFERENCE IN RATES FOR IRREVERSIBLE ISOTOPIC REACTIONS

BY RICHARD B. BERNSTEIN

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois

Received March 6, 1952

The feasibility and usefulness of achieving amplification of the difference in isotopic abundance measured in the course of a competitive isotopic reaction is pointed out. Amplification is accomplished by operating at high extent of reaction and measuring the isotope abundance of the unconverted substrate which is stripped of the lighter isotope by the equivalent of several stages of separation. The over-all separation $S = (k/k^*)^N$, where k/k^* is the ratio of isotopic rate constants and N the equivalent number of stages; $N = -\ln(1 - f)$, where f is the fraction of substrate reacted. Experimental data on the pyrolysis of nickel carbonyl in a flow system and malonic acid in a static system give semi-quantitative confirmation of this result.

A continuous flow method of isotope enrichment is suggested in which the isotopic mixture flows through a reaction zone where preferential reaction occurs, thus concentrating the heavy isotope in the unconverted substrate which may be further enriched in subsequent stages of a cascade. The possible practicality of this approach is considered with the aid of a specific example.

Introduction

Previous work dealing with isotope effects on reaction rates has been primarily concerned with the theory,[1] the implications with regard to the validity of tracer techniques in non-equilibrium systems,[2] and the magnitude of the effects for several of the lighter elements.[3] Except for the isotopes of hydrogen the magnitude of the effect is small, so that high precision in isotopic assay is required to obtain reasonable accuracy in $k/k^* - 1$, the fractional difference in the rates.

The present paper deals with two aspects which have as yet received inadequate attention. First to be considered is the possibility of achieving an amplification of the difference in isotopic abundances measured in the course of a competitive isotopic reaction, thus allowing more precise and convenient determination of the ratio of the rates and adding information at the same time bearing on the kinetic mechanism of the reaction. Second to be presented is a brief analysis of the problem of multi-stage enrichment of isotopes of the lighter elements on the basis of the kinetic effect. This possibility was first suggested by Calvin and Yankwich[4] who patented a method for the enrichment of carbon isotopes based on the difference in decarboxylation rates of isotopic malonic acids. To effect practical separation factors a somewhat cumbersome series of successive decarboxylations and syntheses would be required.

The cases previously studied have involved irreversible reactions carried out for the most part batchwise in a static system. The procedure to be outlined employs a flowing system, better adapted to continuous multi-stage operation.

Description of Method

A mixture of the isotopic molecules is allowed to flow continuously through a zone in which an isotopically preferential reaction occurs. The heavy isotope will tend to be concentrated in the unreacted substrate due to the smaller bond rupture probability. The enriched unreacted material is to be continuously separated from the isotopically depleted products. If desired the reaction products may be converted by a quantitative (non-separative) process into reactant suitable for feed material for a previous stage in a cascade. As an example, consider the competing decomposition reactions

$$\mathrm{AB} \xrightarrow{k} \mathrm{A} + \mathrm{B}$$

$$\mathrm{AB}^* \xrightarrow{k^*} \mathrm{A} + \mathrm{B}^*$$

where A and B represent groups or atoms; the asterisk denotes the heavy isotope, comprising one member of the bond which is ruptured. According to Bigeleisen,[1] the quantity k/k^* could be calculated provided the vibration frequencies for the reactants and activated complex were known. An upper limit for this ratio has been tabulated[2] for many isotopic pairs, assuming the atoms in the complex are essentially unbound. It is possible to calculate a reasonable lower limit for k/k^* on the basis of Slater's[5] treatment for the rupture of an isolated bond, from which one would expect the minimum ratio of rate constants to be $(m^*/m)^{1/2}$, where m is the reduced mass for the pair of atoms connected by the fissile bond.

With this assumption one may calculate the minimum expected value of $k/k^* - 1$ to be

$$\epsilon_0 \equiv \frac{k}{k^*} - 1 = \left(\frac{m^*}{m}\right)^{1/2} \cong \frac{\Delta M}{2M_a}\left(\frac{1}{1 + M_a/M_b}\right)$$

valid for small $\Delta M/M_a$. Here M_a is the mass of the lighter isotopic atom, ΔM the mass difference of the isotopic atoms, and M_b the mass of the other atom of the fissile bond. For a C–C rupture, $\epsilon_0(\mathrm{C}^{13}\text{—}\mathrm{C}^{12}) = 0.021$; for C–I, $\epsilon_0(\mathrm{C}^{13}\text{—}\mathrm{C}^{12}) = 0.038$; for O–C, $\epsilon_0(\mathrm{O}^{18}\text{—}\mathrm{O}^{16}) = 0.027$.

To obtain amplification of these small enrichment factors the simplest device is to allow the reaction to proceed to a *high* extent of completion and examine the isotope ratio of the *undecomposed* substrate, which has been stripped of the lighter isotope with the equivalent of several stages of separation.[5a] Although this may be done in a static system it is more convenient to carry out in a flowing system, suitable for steady-state operation.

If one considers the competing irreversible reactions

$$\mathrm{AB} + \mathrm{C} \xrightarrow{k} \mathrm{P}_1 + \mathrm{P}_2 + \cdots$$

$$\mathrm{AB}^* + \mathrm{C} \xrightarrow{k^*} \mathrm{P}_1^* + \mathrm{P}_2 + \cdots$$

which include as a special case the decomposition reactions, one may write

$$R \equiv -\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{AB}] = k[\mathrm{AB}]^m[\mathrm{C}]^n \cdots$$

---

[1] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[2] J. Bigeleisen, *Science*, **110**, 14 (1949).

[3] See the following, for example, regarding C^{13}: (a) J. Bigeleisen and L. Friedman, *J. Chem. Phys.*, **17**, 998 (1949); (b) J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **29**, 192 (1951); (c) A. A. Bothner-By and J. Bigeleisen, *J. Chem. Phys.*, **19**, 755 (1951); (d) J. Bigeleisen and T. L. Allen, *ibid.*, **19**, 760 (1951).

[4] M. Calvin and P. E. Yankwich, U. S. Patent 2,511,667, June 13, 1950.

[5] N. B. Slater *Proc. Roy. Soc. (London)*, **194**, 112 (1948).

[5a] NOTE ADDED IN PROOF.—Since the completion of this work, a study of a C^{14} isotope effect has been reported by Downes and Harris (*J. Chem. Phys.*, **20**, 196 (1952)) in which the specific activity of the unreacted substrate was measured, and certain equations similar to ours were presented.

and

$$R^* \equiv -\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{AB}^*] = \frac{k^*[\mathrm{AB}^*]}{k[\mathrm{AB}]}R$$

valid for the tracer case. Bigeleisen[2] obtained the general solution of the rate of appearance of tracer in the products. For simple stoichiometry, at small extent of reaction the fractionation in the product is simply the ratio k/k^*; for complete conversion of substrate the final fractionation on the basis of total product is, of course, zero.

If one considers the *unreacted* substrate, however, one may write

$$\frac{\mathrm{d}\ln[\mathrm{AB}]}{\mathrm{d}\ln[\mathrm{AB}^*]} = \frac{k}{k^*} = 1 + \epsilon_1$$

so that

$$\ln S \equiv \ln\frac{[\mathrm{AB}^*][\mathrm{AB}]_0}{[\mathrm{AB}][\mathrm{AB}^*]_0} = -\epsilon_1 \ln\frac{[\mathrm{AB}]}{[\mathrm{AB}]_0};\ \text{valid for } \epsilon_1 \ll 1$$

where S is the over-all separation factor, and the subscript $_0$ refers to the initial conditions. Defining the fractional conversion of substrate $f \equiv 1 - [\mathrm{AB}]/[\mathrm{AB}]_0$, one obtains

$$\frac{\ln S}{\epsilon_1} = -\ln(1 - f)$$

For small over-all separations, defining $\epsilon_N \equiv S - 1$, the above expression becomes $\epsilon_N/\epsilon_1 = -\ln(1 - f) \equiv N$, where N is the number of equivalent stages of separation. For 90% conversion, $N = 2.3$; for 99% and 99.9% $N = 4.6$ and 6.9, respectively. Thus, by proceeding to a large extent of reaction appreciable amplification of the single stage fractionation factor is attainable.

The treatment outlined above should be applicable to any fluid system, but involves the assumption that the rate-limiting step is a separative one involving bond rupture. A factor expected to reduce the separation below that calculated is the possibility of a non-separative governing step in the mechanism, as in the low pressure region in a unimolecular gas decomposition as the transition to a collisional mechanism takes place. One might represent the case of a second order decomposition mechanism by the following set of equations

$$\mathrm{AB} + \mathrm{AB} \xrightarrow{k} \{\mathrm{AB}\} + \mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B} + \mathrm{AB}$$

$$\mathrm{AB} + \mathrm{AB}^* \xrightarrow{k^*} \{\mathrm{AB}\} + \mathrm{AB}^* \longrightarrow \mathrm{A} + \mathrm{B} + \mathrm{AB}^*$$

$$\mathrm{AB}^* + \mathrm{AB} \xrightarrow{k^*} \{\mathrm{AB}\}^* + \mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B}^* + \mathrm{AB}$$

$$\mathrm{AB}^* + \mathrm{AB}^* \xrightarrow{k^{**}} \{\mathrm{AB}^*\} + \mathrm{AB}^* \longrightarrow \mathrm{A} + \mathrm{B}^* + \mathrm{AB}^*$$

Then

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{AB}] = k[\mathrm{AB}]^2 + k^*[\mathrm{AB}][\mathrm{AB}^*]$$

and

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{AB}^*] = k^*[\mathrm{AB}][\mathrm{AB}^*] + k^{**}[\mathrm{AB}^*]^2$$

so

$$\frac{\mathrm{d}\ln[\mathrm{AB}]}{\mathrm{d}\ln[\mathrm{AB}^*]} = \frac{k}{k^*}\ \text{for the tracer case}$$

This yields the same result as for the previously considered situation, but the single stage factor is now the fractional change in the collisional rate constants, which may be an order of magnitude smaller than in the former case, thus giving negligible separation of isotopes even when operating at high conversions. Thus, measurement of the over-all separation obtained at high extent of reaction may conveniently give information on the nature of the rate-determining step. It may be noted that when operating at $f = 0.99$ ($N = 4.6$), an error of 10% in f gives rise to an error of only 2% in the calculated ϵ_1.

Experimental and Results

Several experiments were carried out with a flowing and a static system in an attempt to obtain semi-quantitative confirmation of the amplification principle developed above.

The isotope effect in the thermal decomposition of nickel carbonyl was chosen for preliminary investigation using the flow method. Tank $\mathrm{Ni(CO)_4}$, purified by distillation *in vacuo* immediately before use, was allowed to flow from a reservoir through a Pyrex wool packed tube maintained at temperatures ranging from 70–120° at pressures in the range 10–100 mm. Undecomposed $\mathrm{Ni(CO)_4}$ was separated continuously from CO by means of a trap at −78° or −195°. Flow rates were empirically adjusted so that the fraction of undecomposed $\mathrm{Ni(CO)_4}$ was small. After cutting off the flow and measuring the amount of the recovered $\mathrm{Ni(CO)_4}$, its C^{13} enrichment was determined by pyrolyzing the sample completely and observing mass spectrometrically the m/e 29/28 ratio of the CO. A reference isotope ratio was determined with the CO obtained from complete pyrolysis of a tank sample of $\mathrm{Ni(CO)_4}$.

Several blank runs at low extent of decomposition showed negligible C^{13} enrichment in the undecomposed $\mathrm{Ni(CO)_4}$. Easily measurable enrichments were, however, obtained in two experiments at 108° and 117°, run at 99.5% conversion ($N = 5.3$ stages). Over-all separation factors of 1.20 and 1.16 were obtained, respectively, corresponding to $\epsilon_1 = 0.038$ and 0.030; thus we may take $\epsilon_1 = 0.034 \pm 0.004$. No significance may be attached to the magnitude of the apparent temperature trend due to the rather large probable errors in these preliminary experiments. Examination of the O^{18} abundance revealed no measurable fractionation.

Although the mechanism of this reaction is partly heterogeneous and quite complex,[6] if one postulates that the rate-limiting step is the rupture of a Ni–C bond the data may be interpreted. Consider the elementary steps

$$\mathrm{Ni(CO)_4} \xrightarrow{k_1} \mathrm{Ni(CO)_3}\cdot + \mathrm{CO}$$

$$\mathrm{Ni(CO)_4}^* \xrightarrow{k_2} \mathrm{Ni(CO)_3}\cdot + \mathrm{C^*O}$$

$$\mathrm{Ni(CO)_4}^* \xrightarrow{k_3} \mathrm{Ni(CO)_3}^*\cdot + \mathrm{CO}$$

Thus

$$\ln S \equiv \ln\frac{[\mathrm{Ni(CO)_4}^*][\mathrm{Ni(CO)_4}]_0}{[\mathrm{Ni(CO)_4}^*]_0[\mathrm{Ni(CO)_4}]} = N\epsilon$$

where

$$N = -\ln(1 - f)\ \text{and}\ \epsilon = \frac{k_1}{k_2 + k_3} - 1$$

From theoretical considerations, clearly pointed out by Bigeleisen,[3c] the ratio of rates of reaction of a given substrate into products differing only in isotopic composition should be temperature independent and calculable quite accurately from reduced mass considerations alone. Thus

$$\frac{k_1}{3k_2} - 1 = \frac{\Delta M}{2M_a}\left(\frac{1}{1 + M_a/M_b}\right) = 0.0345$$

Using this value together with the experimental $\epsilon \equiv [k_1/(k_2 + k_3)] - 1 \cong 0.034$ one obtains the quantity $(k_1/4k_2) - 1 \cong 0.059$. This value should

---

(6) C. E. Bawn, *Trans. Faraday Soc.*, **31**, 440 (1935); K. Tonosaki and B. Suginuma, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **22**, 1014 (1943)

theoretically be temperature dependent, decreasing to a high temperature limit equal to the value of $(k_3/3k_2) - 1 = 0.0345$. Further experiments with this reaction are in progress.

In connection with the static method, the decarboxylation of normal malonic acid was chosen because the single stage fractionation factors were obtained previously.[3a,b]

Samples (*ca.* 15 g.) of recrystallized malonic acid (m.p. 137°) were pyrolyzed to completion at 160° in a 30-ml. nickel vessel. After the reaction had ceased the vessel was shut off from the line containing the CO_2 and acetic acid from the last fraction only of the malonic acid. The CO_2 was purified by distillation and examined mass spectrometrically. It was found to be 8.0 ± 1.0% enriched in C^{13}.[7] The over-all separation on the basis of the undecomposed malonic acid is

$$S = \frac{[\mathrm{HOOC^{*}{\cdot}CH_2{\cdot}COOH}][\mathrm{HOOC{\cdot}CH_2{\cdot}COOH}]_0}{[\mathrm{HOOC^{*}{\cdot}CH_2{\cdot}COOH}]_0[\mathrm{HOOC{\cdot}CH_2{\cdot}COOH}]} = \exp(k_1 - k_3 - k_4)t$$

Here the k's are those of Bigeleisen and Friedman.[3a] Defining $\epsilon = k_1/(k_3 + k_4) - 1$, then one obtains $\ln S = N\epsilon$, where $N = -\ln(1 - f)$ as previously.

This should apply to the undecomposed malonic acid; however, in the experiments the last CO_2 fraction was analyzed, so one must consider the (inverse) fractionation of the CO_2 with respect to the malonic acid. For the tracer case one obtains

$$\frac{d[C^{*}O_2]}{d[CO_2]} \cong \frac{2\alpha}{1 - \alpha}\,\frac{k_3}{k_1}\exp(k_1 - k_3 - k_4)t$$

where α is the C^{13} atomic abundance in the normal malonic acid.

Thus $\ln S = N\epsilon + \ln(2k_3/k_1)$. Substituting the experimental values $S = 1.08$, $N = 6.0$, and using Bigeleisen and Friedman's value $k_1/2k_3 = 1.037$, we obtain $\epsilon = 0.020$. This is to be compared with the value $\epsilon = 0.027$ (obtained from their single stage data) and the value 0.033 of Lindsay, *et al.*[3b] The reasons for these discrepancies are not immediately evident; traces of kindred impurities may be responsible.

Discussion

Since it appears possible to obtain several equivalent stages of fractionation by allowing the competing isotopic reactions to proceed to a large extent of completion it is of interest to consider the problem of actual multi-stage operation, *i.e.*, cascading of a large number of single stage separating units.

For the simple type of reaction $AB^{*} \rightarrow A\downarrow + B^{*}$, similar to the $Ni(CO)_4$ decomposition, where AB and B are fluids and A is a solid the system may offer some hope of feasible operation. Assume that physical separation of undecomposed AB and product B may readily be accomplished, and that AB may quantitatively be reformed by combination of B with A under appropriate conditions. Thus the reactions are not strictly irreversible; rather it is possible to select temperatures and pressures such that the equilibria may be displaced far to one side or the other as desired.

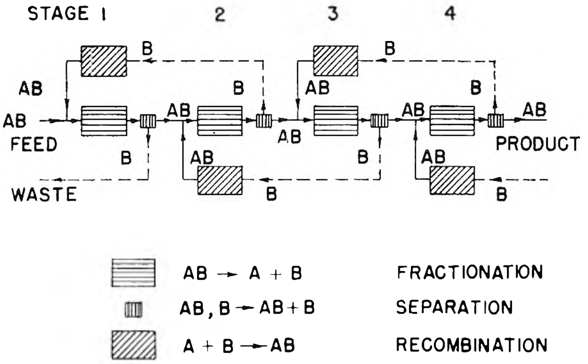


Fig. 1.—Cascade for enrichment of isotopes by difference in rates.

Shown in Fig. 1 is a block diagram of a four-stage section of a cascade intended to effect appreciable over-all separations with more economical utilization of raw material than in the single pass flow system where the greatest portion of feed is discarded.

Cohen[8] has developed the theory of cascade operation of separative units. In the case illustrated by Fig. 1 the input material is fed into the reaction zone of stage 1 at a flow rate such that approximately 50% conversion is obtained in the single traverse. Thus each physical stage is the equivalent of 0.693 ideal stages, for which ϵ_1 may be expected to be of the order of $[\Delta M/2M_a]$ $[1/(1 + M_a/M_b)]$ as discussed previously. The enriched AB^{*} from stage 1 is separated from isotopically depleted B^{*}, combined with re-formed AB^{*} and fed into the next stage. The undecomposed AB^{*} from stage 2 is likewise separated from B^{*} and passed on to stage 3. The depleted B^{*} from stage 1 is discarded; that from stage 3 is passed back through a re-forming cell containing excess $A\downarrow$ at conditions intended to allow quantitative conversion of B^{*} to AB^{*} which is then combined with the enriched AB^{*} from stage 1 and used as feed for stage 2.

From simple considerations one may estimate the size of cascade required to yield, for example, 1 millimole/min. of 10-fold enriched $C^{13}O$ using the $Ni(CO)_4$ reaction. Assuming a single stage factor of $0.693 \times 0.034 = 0.0235$, approximately 100 physical stages would be needed. For an ideal cascade, the flow of feed material required into the first stage is estimated using Cohen's equation (1.11)

$$\frac{L_1}{P} = \frac{(2 + \epsilon)}{\epsilon}\,\frac{(N_p - N_1)}{N_1(1 - N_1)}$$

where L_1/P is the ratio of feed flow to product flow, and N_1 and N_p are mole fractions of desired isotope in feed and product streams. The input flow is thus approximately 0.8 mole/min.

An idea of the total size of the cascade may be obtained by considering the total mass flow into all stages of the cascade. Substituting in Cohen's equation (1.23) the appropriate numerical constants gives for the total flow a value of approximately 30 moles/min.

---

(7) *Cf.* ref. 3b in which a similar experiment was performed, giving 7% C^{13} enrichment at high extent of decomposition.

(8) K. Cohen, "Theory of Isotope Separation," National Nuclear Energy Series III-1B, McGraw-Hill Book Co., Inc., N. Y., 1951.

It should be noted that the inventory of nickel remains constant in the steady state, but that periodic interchange of function of reaction cells and re-forming cells is required. The major drawback to the success of the above isotope enrichment scheme would seem to be the problem of control for such a complex cascade.

A homogeneous reaction whose kinetic behavior is reproducible would be highly desirable, in order to allow prediction of appropriate flow rates per stage for 50% conversion in a single pass at a given temperature. It appears improbable that the method described would ever compete with conventional countercurrent chemical exchange methods from the viewpoint of feasibility and efficiency.

Acknowledgment.—This research was supported in part, by the U. S. Atomic Energy Commission.

DISCUSSION

J. BIGELEISEN (Brookhaven Nat. Lab.).—Lindsay, Bourns and Thode have redetermined the intramolecular isotope effect in the decarboxylation of malonic acid (*Canadian Journal of Chemistry*, **30**, 163 (1952)). Their recent and more extensive results are in quantitative agreement with those reported by Bigeleisen and Friedman (*J. Chem. Phys.*, **17**, 998 (1949)). It is interesting to note that Bernstein's multistage experiment on malonic acid, similar to the one carried out by Lindsay, Bourns and Thode, gives a value for the isotope effect in substantial agreement with that obtained previously by single stage experiments. This provides an additional confirmation of the theory.

R. B. BERNSTEIN.—Due to the large effect of traces of kindred impurities upon the apparent enrichment of unreacted substrate measured at high extent of reaction, it would not seem advisable to place the same confidence in the results of such multistage experiments as in those of the more reliable single stage measurements, however.

G. M. HARRIS (University of Wisconsin).—It is important to emphasize that the mathematical treatment given here and in our own paper for isotopic enrichment effects resulting from reaction rate differences is by no means general. The rate law must be of a simple enough form and the concentration of tracer isotope low enough that the reaction can be always assumed to be first order with respect to concentration of labelled molecules.

Isotopic enrichment by the procedure outlined by Professor Bernstein has interesting practical possibilities in the case of the nearly complete decomposition of a large quantity of a cheap reactant. Has anyone, for example, examined the last portion of CO_2 from the calcination of a large batch of limestone for possible C^{13} enrichment?

BERNSTEIN.—In the paper of Bigeleisen [*Science*, **110**, 14 (1949)] it is pointed out that the isotopic reaction will always be first order in the tracer isotope regardless of the rate law for the over-all reaction. This is seen from consideration of the physical situation: the rate of occurrence of events which lead to reaction for the isotopically labelled molecules is proportional to the number of these remaining, since the probability of interaction between two or more labelled molecules is negligible, at the tracer level.

Regarding the last comment, it may be noted that even after the decomposition of all but $10^{-8}\%$ of reactant, only 23 equivalent stages of enrichment are obtained. Thus one should not expect gross separation of carbon isotopes, even under the most favorable circumstances.

THE ISOTOPE EFFECT IN THE DECOMPOSITION OF OXALIC ACID[1,2]

BY ARTHUR FRY[3] AND MELVIN CALVIN

Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

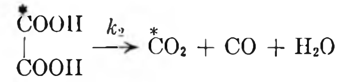
Received March 6, 1952

The C^{13} and C^{14} isotope effects in the decomposition of oxalic acid have been studied simultaneously at two different temperatures. In each case the C^{14} effect is approximately double the C^{13} effect, and both are in reasonable accord with theoretical calculations based on a simple postulated mechanism for the reaction.

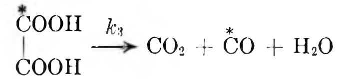
Introduction

Lindsay, McElcheran and Thode[4] have studied the C^{13} isotope effect in the decomposition of oxalic acid in concentrated sulfuric acid at 100°. The results were reported as ratios of rate constants for the equations

$$(COOH)_2 \xrightarrow{k_1} CO_2 + CO + H_2O \qquad (1)$$



$$\overset{*}{C}OOH\text{—}COOH \xrightarrow{k_2} \overset{*}{C}O_2 + CO + H_2O \qquad (2)$$



$$\overset{*}{C}OOH\text{—}COOH \xrightarrow{k_3} CO_2 + \overset{*}{C}O + H_2O \qquad (3)$$

The ratio k_2/k_3, where C^* indicates C^{13}, was found to be 1.032, while $k_1/(k_2 + k_3)$ was 1.034.

Similar experiments have now been carried out using oxalic acid-1,2-$C_2{}^{14}$, and both the C^{13} and the C^{14} isotope effects have been determined on the same samples. In addition, the decompositions have been carried out at two different temperatures, and the differences in heat and entropy of activation for decomposition by equations (2) and (3) have been calculated for both C^{13} and C^{14}.

Experimental

Preparation of Oxalic Acid-1,2-C_2^{14}.—The oxalic acid-1,2-C_2^{14} used was prepared by the reaction between carbon dioxide-C^{14} and potassium on sand at 360°.[5] The product from this reaction was purified by alternate calcium oxalate precipitations and continuous ether extractions. In the final step of the purification the ether extract was evaporated over a small amount of water. The solution was filtered and the water was removed by lyophilization, leaving a pure white product of anhydrous oxalic acid-1,2-C_2^{14}. Yields were from 45–55% with an additional 15–20% of the activity being recovered undiluted as carbon dioxide. The oxalic acid was checked for radioactive impurities by paper strip chromatography using a mixture of *t*-amyl alcohol and benzene saturated with 3 *N* hydrochloric acid as the solvent. No radioactive spots were found except for the oxalic acid spot, and an upper limit of 0.5% was set for the amount of radioactive impurity. An inactive sample prepared by the same procedure gave theoretical equivalent weight values when titrated with either base or permanganate. For use in the decomposition experiments, a sample of the oxalic acid-1,2-C_2^{14} was diluted with specially purified inactive oxalic acid by dissolving the two samples together, filtering and removing the water by lyophilization.

Preparation of ~100% Sulfuric Acid.—The ~100% sulfuric acid used was prepared by adding 100 cc. of 30% fuming sulfuric to 150 cc. of ordinary concentrated sulfuric acid in a glass stoppered flask. The solution was shaken vigorously and allowed to stand overnight. A sample of 1 cc., wt. = 1.8214 g., was diluted with water and upon titration with standard 1 *M* sodium hydroxide required 36.92 cc. for neutralization, giving a molecular weight of 97.5 (99.4% of theory). This same sulfuric acid stock was used in all the decomposition experiments.

Decomposition Experiments.—The decompositions were carried out using 99.4% sulfuric acid in the apparatus shown in Fig. 1. Approximately one-gram samples of oxalic acid were placed in the decomposition chamber, B. The apparatus was assembled, using the 99.4% sulfuric acid to lubricate the joints and stopcocks. Ten cc. of the 99.4% sulfuric acid was pipetted into the preheater, C, and dry carbon dioxide-free oxygen was allowed to sweep through the system for about one hour. The gas from the outlet of the assembly shown in Fig. 1 was conducted, in turn, through a spiral trap cooled by a Dry Ice–isopropyl alcohol mixture, a spiral bubbler filled with 2 *M* sodium hydroxide to remove the carbon dioxide, a copper oxide-packed furnace at ~700° to burn the carbon monoxide to carbon dioxide, and another sodium hydroxide filled bubbler to absorb this carbon dioxide. When the oxygen had been sweeping through the apparatus for about an hour, the spiral bubblers were filled with 2 *M* sodium hydroxide, and the liquid in flask A was heated to reflux by means of a Glas-col mantle.

The vapor of the boiling liquid served as a constant tem-

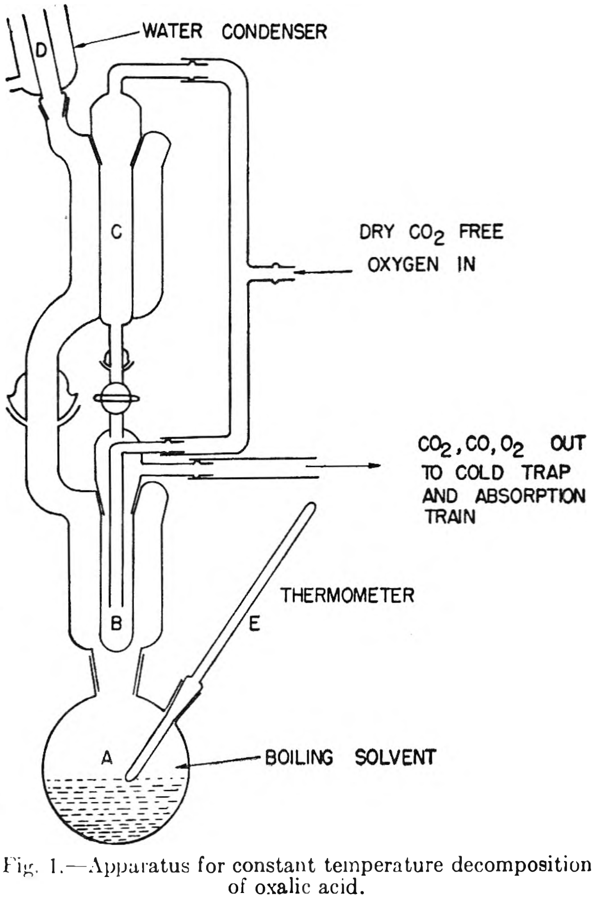


Fig. 1.—Apparatus for constant temperature decomposition of oxalic acid.

---

[1] The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

[2] This paper was abstracted from part of the thesis submitted by Arthur Fry to the Graduate Division of the University of California in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.

[3] Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

[4] J. G. Lindsay, D. E. McElcheran and H. G. Thode, *J. Chem. Phys.*, **17**, 589 (1949).

[5] F. A. Long, *J. Am. Chem. Soc.*, **61**, 570 (1939).

perature bath to heat the sulfuric acid and oxalic acid to the desired reaction temperature. The boiling point of the liquid in flask A determined the temperature of decomposition. Dioxane and carbon tetrachloride were chosen to give temperatures of 103.0 and 80.1°, respectively. When the liquid in flask A had been refluxing vigorously for approximately one-half hour, the stopcock was opened and the sulfuric acid was allowed to flow onto the oxalic acid. At 103.0° the reaction was very vigorous and care had to be exercised in adding the sulfuric acid to avoid frothing. In all cases the sulfuric acid was added as rapidly as possible. The oxygen sweep served to stir the oxalic acid–sulfuric acid mixture. The sweep was continued until gas bubbles were no longer observed in the sulfuric acid solution, and then for an additional hour and one-half. The carbonate in the two bubblers was collected and weighed as barium carbonate. The yields of barium carbonate from the carbon dioxide and carbon monoxide were quantitative, and the blanks were negligible.

Isotopic Composition Measurements.—The C^{14} activity measurements were made using an ionization chamber and vibrating reed electrometer connected to a Brown recorder. The ionization chambers were filled to a standard pressure with carbon dioxide generated in a vacuum system from the barium carbonate with concentrated sulfuric acid. A sample of this same carbon dioxide was stored in a bulb for later mass spectrometric analysis. The samples from the carbon monoxide and carbon dioxide from a given run were measured in immediate succession in the same ionization chamber and on the same instrument in order to reduce to a minimum any variations in the procedure and instruments. Several independent measurements were made on each sample from each decomposition, starting with the barium carbonate in each case.

The C^{13} measurements[6] were made on a Consolidated Type 21-102 mass spectrometer, using a magnetic sweep to scan the peaks at $m/q = 44$ and 45. Several independent scannings of each sample were made. In several cases, the entire low m/q mass spectrum was taken using a voltage scan, and no peaks were found except those of the normal carbon dioxide pattern. Samples of normal carbon dioxide were also run during the sample determinations to check the reproducibility of the mass spectrometer. The $m/q = 45$ peak height was corrected for the O^{17} content of the carbon dioxide.

Results

The $C^{14}O_2$ specific activities and $C^{13}O_2$ mole fractions obtained in the various runs are shown in Table I. In all cases, the values given are averages of several measurements, and the indicated errors are average deviations of these measurements.

TABLE I

$C^{14}O_2$ SPECIFIC ACTIVITIES AND $C^{13}O_2$ MOLE FRACTIONS FROM THE DECOMPOSITION OF OXALIC ACID-1,2-C_2^{14}

$H_2C_2O_4$ Decomposition Run No.	Temp., °C.	C^{13} Mole fraction $\frac{C^{13}O_2{}^a}{C^{12}O_2 + C^{13}O_2} \times 10^6$ CO_2 Fraction	C^{13} Mole fraction $\times 10^6$ CO Fraction	C^{14} Specific activity[b] Drift rate, volts/min. $\times 10^3$ CO_2 Fraction	C^{14} Specific activity[b] Drift rate, volts/min. $\times 10^3$ CO Fraction
1	103.0	1089 ± 6	1065 ± 3	4585 ± 40	4336 ± 29
2		1092 ± 0	1058 ± 2	4535 ± 39	4277 ± 37
Normal CO_2					
1		1115 ± 1			
3		1088 ± 2	1059 ± 4	4554 ± 39	4328 ± 68
4		1091 ± 3	1062 ± 5	4504 ± 27	4286 ± 29
Normal CO_2					
2		1116 ± 1			
Permanganate oxidation		1074 ± 2		4432 ± 36	
5	80.1	1114 ± 1	1076 ± 3	4507 ± 21	4203 ± 36
6		1110 ± 2	1078 ± 6	4636 ± 43	4335 ± 31
Normal CO_2					
3		1137 ± 3			
7		1107 ± 3	1073 ± 3	4531 ± 11	4247 ± 20
8		1110 ± 2	1075 ± 3	4614 ± 17	4352 ± 24
Normal CO_2					
4		1136 ± 1			

[a] Corrected for presence of $C^{12}O^{17}O^{16}$. [b] Actual specific activity = ~30 dis./min./mg. $BaCO_3$.

The C^{13} measurements were made at two different times, runs 1–4 and normal carbon dioxide 1 and 2 (carbon dioxide from Dry Ice) being measured at one time and runs 5–8 and normal carbon dioxide 3 and 4 (same stock sample of carbon dioxide) being measured somewhat later.

Since in the subsequent calculations, only the relative $C^{13}O_2$ fractions are used, the variation in normal carbon dioxide value between the two times is not serious since the difference is reflected in the values from both the carbon monoxide and carbon dioxide. The C^{14} measurements were made using different instruments and at different times which probably accounts for the variations in specific activity from run to run. However, the carbon dioxide and carbon monoxide fractions from the same run were measured in immediate succession on the same instrument to reduce this variation as much as possible within a given run.

In the following calculations only the monolabeled oxalic acid is considered although the oxalic acid actually used is called oxalic acid-1,2-C_2^{14}, since by its method of preparation both carbon atoms would be labeled if pure $C^{14}O_2$ were used. Actually, the number of dilabeled molecules was calculated to be a very negligible fraction of the total.

Referring to equations (1), (2) and (3) and assuming that the reaction is first order with respect to oxalic acid, the specific activities or mole fractions of the carbon dioxide and carbon monoxide are given by the following equations, where Ox refers to oxalic acid containing only C^{12} and Ox* refers to oxalic acid containing C^{13} or C^{14}

$$\frac{C^*O_2}{C^*O_2 + CO_2} = \frac{k_2}{k_2 + k_3}\,\frac{Ox^*(1 - e^{-(k_2+k_3)t})}{Ox(1 - e^{-k_1t}) + Ox^*(1 - e^{-(k_2+k_3)t})}$$

and

$$\frac{C^*O}{C^*O + CO} = \frac{k_3}{k_2 + k_3}\,\frac{Ox^*(1 - e^{-(k_3+k_3)t})}{Ox(1 - e^{-k_1t}) + Ox^*(1 - e^{-(k_2+k_3)t})}$$

Combining the above equations gives equation (4)

$$\frac{C^*O_2}{C^*O_2 + CO_2}\Big/\frac{C^*O}{C^*O + CO} = \frac{k_2}{k_3} \qquad (4)$$

It should be noted that k_2/k_3 calculated in this manner is independent of time, and hence of the amount of reaction, while comparing the specific activity of the carbon dioxide or carbon monoxide to that of the oxalic acid is not.

For ease of tabulation and convenience of reference, the percentage isotope effect may be defined as $100\ (k_2/k_3 - 1)$. The percentage isotope effect values calculated by equation (4) from the data in Table I are given in Table II. The data of Lindsay, McElcheran and Thode[4] have been recalculated in this manner, and show a much narrower spread than using their method of calculation, although the average

TABLE II

C^{13} AND C^{14} ISOTOPE EFFECT IN THE DECOMPOSITION OF OXALIC ACID

Decomposition Run No.	Temp., °C.	Per cent. isotope effect $100(k_2/k_3 - 1)$ C^{13}	Per cent. isotope effect $100(k_2/k_3 - 1)$ C^{14}
1	103.0	2.3	5.7
2		3.2	6.0
3		2.7	5.2
4		2.7	5.1
Average		2.7 ± 0.22	5.5 ± 0.30
5	80.1	3.5	7.2
6		3.0	6.9
7		3.2	6.7
Average		3.25 ± 0.15	6.7 ± .35
Lindsay, McElcheran and Thode[a]			
1	100	2.9	
2		3.5	
Average		3.2	

[a] Recalculated from the original data using equation (4).

---

(6) Thanks are due to Dr. A. Newton and Dr. L. Tolman of this Laboratory for these measurements.

values are the same. These recalculated values are also shown in Table II.

Discussion

The C^{13} isotope effect values shown in Table II are thus in very satisfactory agreement with the results obtained by Lindsay, McElcheran and Thode.[4] The C^{14} effect is approximately double the C^{13} effect at each temperature.

The differences in heat and entropy of activation caused by the isotopic substitution can be calculated from the theory of absolute rates.[7]

For equation (2), and temperature T_1

$$(k_2)_{T_1} = \frac{kT_1}{h} e^{\Delta S_2^{\ddagger}/R}\, e^{-\Delta H_2^{\ddagger}/RT}$$

and for equation (3), and T_1

$$(k_3)_{T_1} = \frac{kT_1}{h} e^{\Delta S_3^{\ddagger}/R}\, e^{\Delta H_3^{\ddagger}/RT}$$

Combining

$$\left(\frac{k_2}{k_3}\right)_{T_1} = e^{(\Delta S_2^{\ddagger} - \Delta S^{\ddagger})/R} e^{-(\Delta H_2^{\ddagger} - \Delta H_3^{\ddagger})/RT} \qquad (5)$$

In a similar manner an equation is set up for T_2, and when this equation is combined with (5), equation (6) results

$$\frac{(k_2/k_3)_{T_1}}{(k_2/k_3)_{T_1}} = e^{-\frac{(\Delta H_2^{\ddagger} - \Delta H_3^{\ddagger})(T_2 - T_1)}{RT_1T_2}} \qquad (6)$$

From the data in Table II, $(\Delta H_2^{\ddagger} - \Delta H_3^{\ddagger})$ can be calculated by equation (6), and this value can be substituted back into equation (5), and $(\Delta S_2^{\ddagger} - \Delta S_3^{\ddagger})$ can be calculated. The calculated values are shown in Table III.

TABLE III

HEAT AND ENTROPY OF ACTIVATION DIFFERENCE BETWEEN EQUATIONS (2) AND (3)

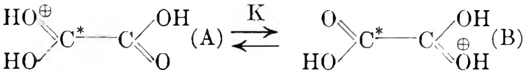
Isotope	$-(\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_3)$, cal./mole	$(\Delta S^{\ddagger}_2 - \Delta S^{\ddagger}_3)$, e.u.
C^{13*}	61	−0.11
C^{14}	131	−0.24

The presence of the isotope effect measured here allows some rather specific conclusions to be drawn concerning the mechanism of the decomposition.[8] At complete reaction, all of the carbon–carbon bonds, in all the molecules, are broken, so the isotope effect observed cannot be due to isotopic discrimination in the rate of rupture of the carbon–carbon bonds.

Therefore, if the observed isotopic fractionation is due to an isotope effect in the rate-determining step of the reaction, the rate-determining step must be the breaking of a carbon–oxygen bond, since the association of hydrogen with oxygen is commonly considered to be rapid and reversible.

However, the observed isotope effect might also be due to some equilibrium step. An isotope effect is conceivable in rapid steps following the rate-determining step only under very special circumstances. These require a symmetrical starting molecule and either a symmetrical product of the rate-determining step or products which are rapidly interconvertible compared to the irreversible following reactions, in which the isotope selection is made. If an equilibrium process occurs before the rate-determining step, an isotope effect in the equilibrium could multiply an isotope effect in the rate-determining step. Such a multiplication of effects could conceivably lead to either a larger or smaller overall effect, depending on whether the equilibrium constant was greater or less than one. Several such pre-equilibria might be involved in some cases.

In the present case a reasonable equilibrium prior to the rate determining step might be the association of a hydrogen ion with one of the carbonyl groups of the acid as shown in equation (7).



(7)

A simple calculation of the equilibrium constant, K, may be made using the equations derived by Bigeleisen and Mayer[9] or by Urey.[10] For lack of complete data, we have assigned the frequency of 1750 cm.$^{-1}$ to the C=O vibration, 1100 cm.$^{-1}$ to the normal C—O vibration and 1500 cm.$^{-1}$ to the two C⋯OH vibrations which are hybridized by resonance. The isotopic shifts are then calculated using the approximation of simple harmonic oscillators. Using these values the equilibrium constant at 100° is calculated to be 0.988 for C^{14} substitution and 0.995 for C^{13} substitution. Thus this particular equilibrium decreases the calculated isotope effect, but it is conceivable that in other cases the effect would be in the opposite direction.

In calculating the ratio k_2/k_3, the above vibrational frequencies are assigned to the normal molecules (A) and (B). For the transition state we take a model in which water has been lost from the carbon originally attached to two OH groups and the carbon–carbon bond is greatly weakened leaving nearly free molecules of carbon monoxide and $^{\oplus}$COOH. The carbon monoxide is assigned its accepted frequency of 2170 cm.$^{-1}$ and the carbonyl and hydroxyl frequencies in $^{\oplus}$COOH are assumed to be unchanged. The force constant for the C⋯OH bond which is broken is set equal to zero. The ratio k_2/k_3 is then calculated using equation (8), as derived by Bigeleisen.[11]

$$\frac{k_2}{k_3} = \left(\frac{\mu_3}{\mu_2}\right)^{1/2}\left[1 + \sum_{i}^{3n-6} G(u_i)\Delta u_i - \sum_{i}^{3n-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right] \qquad (8)$$

The function G(u) is defined by Bigeleisen and Mayer[9] who have tabulated values of G(u) as a function of u. The reaction coördinate reduced mass, μ, is assumed to be the reduced mass of the atoms forming the bond being broken. The symbol ‡ refers to the activated complex.

The rate ratio, k_2/k_3, calculated in this manner, when multiplied by the equilibrium constants calculated above, give over-all isotope effects of

---

(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(8) The authors wish to express their thanks to Prof. Richard Powell for a fruitful discussion of the mechanism of the decomposition.

(9) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

(10) H. C. Urey, *J. Chem. Soc.*, 562 (1947).

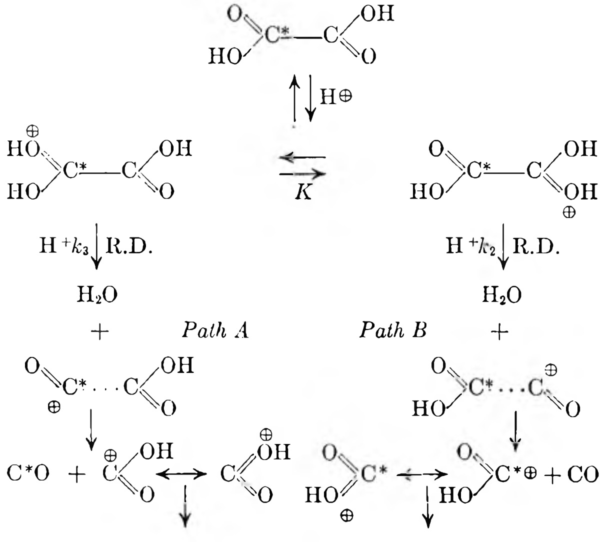
(11) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

6.0% for C^{14} substitution and 3.1% for C^{13} substitution at 100°. These compare to the values of 5.5% and 2.7% measured experimentally. The corresponding calculated values at 80° are 6.3 and 3.4% compared to the experimental values of 6.7 and 3.25%.[12] The agreement in magnitude is quite satisfactory, but the calculated temperature coefficient is not large enough to explain that observed experimentally. Perhaps a better choice of frequencies and model would lead to a more satisfactory calculation. Ultimately the study of isotope effects in chemical reactions should enable us to elucidate all of the intimate details of the mechanism of the reaction. When the proper equilibria and rate determining steps are chosen, the calculated isotope effect should coincide with that observed experimentally. The choice of a molecule which reacts at one of two chemically identical groups, such as oxalic or malonic acid is a fortunate one, since net isotope effects are observed at complete reaction, thus making it unnecessary to study the isotopic composition of the products as a function of the amount of reaction.

The presence of an isotope effect does not unequivocally establish the mechanism of the decomposition, but it does offer very strong evidence that the rupture of the carbon–carbon bond is not rate determining, and, consequently, that the rate-determining step in this medium is the rupture of the carbon–oxygen bond. Actually, the rupture of the carbon–oxygen bond and of the carbon–carbon bond is probably all part of a concerted reaction with the loss of hydroxyl (or water) from one carboxyl or the other being the initiating step. The essential steps of what is considered to be the most likely mechanism for the decomposition are shown in Chart I.

Path A is seen to be less likely than Path B, since we observe an enrichment of labelled atoms in the carbon dioxide.

Chart I.—Mechanism of the Decomposition of Oxalic Acid in 100% Sulfuric Acid



DISCUSSION

J. BIGELEISEN (Brookhaven Nat. Lab.).—It is quite interesting to note that Fry and Calvin find the quantity $(k_2/k_3 - 1)C^{12}, C^{14}/(k_2/k_3 - 1)C^{12}, C^{12}$ equal to 2.0 within the limits of experimental error. This is in accord with the theoretical expectations as discussed in my paper earlier in the symposium. In footnote (12) it is suggested that nuclear spin effects may be responsible for the deviation of this quantity in the work of Stevens, Pepper and Lounsbury, and Yankwich, Stivers and Nystrom. It has been pointed out several times previously in the present symposium that no effects due to nuclear spin can be observed in chemical reactions involving the isotopes of carbon and carried out at temperatures above 10°K.

It is improper to calculate an effect of isotopic substitution on the entropy of activation from equation (5). From equation (8) or equation (5) of my paper (*J. Chem. Phys.*, **17**, 675 (1949)) one finds that the difference in entropies of activation should be calculated after the "reduced mass effect" has been factored out. Equation (5) in the paper by Fry and Calvin should have the factor $(M_3/M_2)^{1/2}$ multiplied into the right-hand side. I am preparing a paper for publication which discusses the effect of isotopic substitution on the entropy, enthalpy and heat capacity of equilibrium systems and the similar quantities in reaction rates. There will be extensive tables for the calculation of these quantities from molecular data.

It is interesting to note, in connection with the calculation of k_2/k_3, that the major contribution comes from the factor $(M_3/M_2)^{1/2}$. Am I correct in assuming that the frequency shifts are calculated by assuming that Slater's theorem applies to all the vibrations? Slater has shown this to be approximately true for just one frequency, but not all. In fact, if it were assumed to be true for all frequencies, the product rule would be violated.

A similar objection can be raised to the acid–base equilibrium calculation. The result in this case is close to what is predicted for acid-base isotopic exchange equilibria (*cf.* ref. 9) and is quite insensitive to the absolute value of $\Sigma G(u)\Delta u$ for either the acid or base pair.

A. FRY.—The frequency shifts for those frequencies which are not assumed to be unchanged are calculated using the

---

(12) We have recently learned, by private communication, of experiments in two other places (Research Chemistry Division, Atomic Energy Project, National Research Council, Chalk River, Canada; and Department of Chemistry, University of Illinois) in which the isotope effect in a chemical reaction was determined for both C^{13} and C^{14} simultaneously on the same reaction. In both of these cases the reported C^{14} effect is much more than twice the C^{13} effect. The results for the decomposition of mesitoic acid given by Stevens, Pepper and Lounsbury (Canada), *J. Chem. Phys.*, **20**, 192 (1952), are as follows: k_{12}/k_{13} 1.038 ± 0.003; k_{12}/k_{14} 1.101 ± 0.005. Here the C^{14}/C^{13} ratio is almost three. The results reported by Yankwich, Stivers and Nystrom (Illinois) at the Berkeley Meeting of the American Physical Society in December, 1951, and mentioned in the Abstract appearing in the Bulletin of the American Physical Society, **26**, No. 8, Paper B5, give values for both the C^{13} and C^{14} effects corresponding with those previously reported. Here the C^{14} effect is about four times the size of that for C^{13}. This latter report was for the decarboxylation of malonic acid at its melting point. It is clear that from these three comparative studies, if results are accepted on their face value, that there are isotope factors involved in the determination of the rate of these decarboxylation reactions of which we are not yet cognizant, since it is difficult to see how a change in mass from C^{13} to C^{14} could change the mechanism of the reaction, unless perhaps nuclear spin were involved in some way.

approximation that the bond may be considered as a simple harmonic oscillator between the two atoms forming the bond. This is probably no worse an approximation than others involved, such as the arbitrarily chosen frequency assignments. The calculated and experimental values are both considerably larger than the reduced mass term by itself.

P. E. Yankwich (University of Illinois).—I believe that we all agree that the statistical rate theory cannot permit a ratio of C^{14} and C^{13} intramolecular isotope effects which is sensibly greater than 2. It should be pointed out, however, that within this limitation we are still permitted considerable latitude in the choice of a detailed model, and, as Dr. Fry has shown, it is possible to construct reasonable models which are not in agreement with either the C^{13} or C^{14} experiments on some compounds.

One of the compounds which has been studied by several groups of workers is unsubstituted malonic acid. There is apparent agreement on the values for the C^{13} isotope effects and no agreement on the values obtained with C^{14}. Mr. E. C. Stivers and I have completed recently redeterminations of the intramolecular isotope effects in the decarboxylation of C^{13} and C^{14} labeled malonic and bromomalonic acids. The results for C^{14} (expressed in the notation introduced by the Chairman) are: $100(k_4/k_3 - 1) = 9.9 \pm 0.6$ (malonic) and 11.6 ± 0.6 (bromomalonic); the corresponding results with C^{13} are 2.8 ± 0.3 and 2.4 ± 0.4. The stable isotope results with bromomalonic acid leave much to be desired, but the very much greater than 2 experimental ratio of C^{14} to C^{13} isotope effects is shown clearly.

In the matter of agreement among various workers on the magnitudes of these effects, it is interesting to note that H. G. Thode and his co-workers report C^{13} intramolecular isotope effects which differ by almost 30% for two different samples of commercial malonic acid. The sample which gave the higher effect was analyzed carbon-by-carbon and found to be isotopically homogeneous. With the permission of the Chairman and of Dr. Thode, I would like to ask Dr. Thode if one of his reported values is to be favored over the other, or if the difference between them can be attributed to experimental error.

H. G. Thode.—The difference in the C^{13} intramolecular isotope effect for two commercial samples of malonic acid reported by us (Lindsay, Bourns and Thode) and referred to by Dr. Yankwich, we believe is real. As suggested in our paper, this difference could be explained by a depletion of only 0.5% in the C^{13} content of the methylene carbon of the British Drug House malonic acid. We would favor the result obtained with Eastman Kodak Co. malonic acid since the C^{13} content of the methylene carbon was checked in this case and found to be very nearly the same as that for the CO_2 from the completely oxidized malonic acid.

THE C^{14} ISOTOPE EFFECT IN THE DECARBOXYLATION OF α-NAPHTHYL- AND PHENYLMALONIC ACIDS[1,2]

By Arthur Fry[3] and Melvin Calvin

Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

Received March 6, 1952

The isotope effects in the decarboxylation of α-naphthylmalonic acid-1-C^{14} and phenylmalonic acid-1-C^{14} have been measured, both in solution and on the liquid acids near their melting points. The carboxyl group containing C^{12} is lost as carbon dioxide about 10% more frequently than is the C^{14}-containing carboxyl group. Some aspects of the theoretical calculations of intramolecular isotope effects are considered. Neither the models considered here nor the previously proposed models of Bigeleisen give agreement between theory and experiment for both the C^{13} and C^{14} cases.

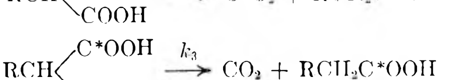
Introduction

In recent years the question of the effect of the substitution of isotopic carbon on the rate of chemical reactions has received considerable attention. A considerable portion of this attention has been directed toward determining the isotope effect in the decarboxylation of malonic acids. Yankwich and Calvin[4] studied the decarboxylation of malonic acid-1-C^{14} and bromomalonic acid-1-C^{14}, and found rupture ratios for C^{12}–C^{12} bonds to C^{14}–C^{12} bonds of 1.12 ± 0.03 and 1.41 ± 0.08, respectively. The authors mentioned that the bromomalonic acid case was a single experiment on acid of doubtful purity.[5]

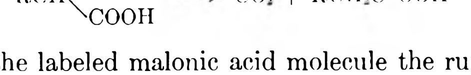
Since this time considerable work has been done on malonic acid, both experimentally[5–8] and theoretically.[9–11]

The decarboxylation of a malonic acid may be represented by the following equations where C* represents C^{13} or C^{14}

$$\mathrm{RCH(COOH)_2} \xrightarrow{k_1} \mathrm{CO_2 + RCH_2COOH} \qquad (1)$$



$$\mathrm{RCH}\left\langle\begin{matrix}\mathrm{C^*OOH}\\ \mathrm{COOH}\end{matrix}\right. \xrightarrow{k_2} \mathrm{C^*O_2 + RCH_2COOH} \qquad (2)$$



$$\mathrm{RCH}\left\langle\begin{matrix}\mathrm{C^*OOH}\\ \mathrm{COOH}\end{matrix}\right. \xrightarrow{k_3} \mathrm{CO_2 + RCH_2C^*OOH} \qquad (3)$$

For the labeled malonic acid molecule the rupture ratio C^{12}–C^{12}/C^{14}–C^{12} is given by the ratio k_2/k_3. In the terminology of Lindsay, Bourns and Thode,[7] this is an intramolecular isotope effect.

---

(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) This paper was abstracted from the thesis submitted by Arthur Fry to the Graduate Division of the University of California in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.

(3) Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

(4) P. E. Yankwich and M. Calvin, *J. Chem. Phys.*, **17**, 109 (1949).

(5) The bromomalonic acid case has recently been checked and the ratio found to be around 1.1 rather than 1.4; P. E. Yankwich, E. C. Stivers and R. F. Nystrom, *J. Chem. Phys.*, **20**, 344 (1952).

(6) J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

(7) J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **29**, 192 (1951).

(8) A. Roe and M. Hellmann, *J. Chem. Phys.*, **19**, 660 (1951).

(9) J. Bigeleisen, *ibid.*, **17**, 425 (1949).

(10) K. Pitzer, *ibid.*, **17**, 1341 (1949).

(11) A. A. Bothner-By and J. Bigeleisen, *ibid.*, **19**, 755 (1951).

Bigeleisen's calculations[9] lead to values for k_3/k_2 of 1.020 for C^{13} substitution and 1.038 for C^{14} substitution. Pitzer's calculations[10] are not applicable to the ratio k_3/k_2, as was pointed out by Bothner-By and Bigeleisen.[11] Actually Pitzer's calculations constitute an evaluation of $k_1/2k_2$.

Bigeleisen and Friedman[6] studied the C^{13} isotope effect in the decarboxylation of malonic acid of normal isotope composition. The observed value corresponding to k_3/k_2 was found to be 1.020. For this same ratio, Lindsay, Bourns and Thode[7] obtained values of 1.021 and 1.026 on two different samples of malonic acid. The C^{13} experimental value reported by Yankwich, Stivers and Nystrom[5] is 1.026. Yankwich and Calvin's[4] value for k_3/k_2 in the C^{14} case was 1.12. Roe and Hellmann[8] reported a value of 1.06. Yankwich, Stivers and Nystrom[5] obtained a value of 1.099 for malonic acid and a slightly larger value for bromomalonic acid.

The agreement among the values determined by the various workers in the C^{13} case is reasonably good, and the agreement between these values and Bigeleisen's calculated value[9] is satisfactory. No such agreement is found between calculation and experiment in the C^{14} case. All of the C^{14} values are higher than the calculated value, in some cases by a factor of two or three.

A desirable way to check these large C^{14} values would be to study an acid which would be expected to give an even larger effect than malonic acid itself. Apparently, the bromo substituent in bromomalonic acid causes such an effect. From zero point energy considerations, a larger isotope effect would be expected with an acid which decarboxylates at a lower temperature.

Another very desirable characteristic for a suitable malonic acid would be ease of purification of the malonic acid itself and of the substituted acetic acid derived from it.

Blicke and Feldkamp[12] have prepared a series of α-naphthylalkylacetic acids by hydrolysis and decarboxylation of the corresponding α-naphthylalkylmalonic esters. They state that addition of acid to an aqueous solution of the potassium salt of the malonic acid at room temperature results in the precipitation of the malonic acid as an oil which spontaneously loses carbon dioxide, forming the corresponding acetic acid.

Such acids would be nearly ideally suited to a study of the isotope effect in the decarboxylation of the malonic acid. A large group is present such as in bromomalonic acid; the acids apparently decarboxylate at room temperature; the substituted acetic acids produced are stable and readily purified.

On investigation of the alkaline hydrolysis of α-naphthylmalonic ester it soon became apparent that the carbon dioxide evolution upon addition of acid was not due to decarboxylation of the malonic acid, but rather to carbonate caused by basic cleavage of the ester.[13]

The free α-naphthylmalonic acid, however, did decarboxylate in solution at relatively low temperatures, so it was decided to carry out isotope effect experiments using it. Later the isotope effect in the decarboxylation of phenylmalonic acid was also studied.

Procedure and Results

The substituted malonic esters were prepared by condensation of diethyl oxalate with the substituted acetic ester, and decarbonylation of the resulting glyoxylate. The most satisfactory hydrolysis procedure was found to be transesterification of the malonic ester with acetic acid catalyzed by hydrochloric acid.[14]

α-Naphthylmalonic acid and phenylmalonic acid were decarboxylated in the liquid state near the melting points, and in dioxane–1 *N* hydrochloric acid solution at 72.8° and at 87.5°. The carbon dioxide evolved was collected as barium carbonate. The α-naphthyl- and phenylacetic acids were purified, and samples of them and of the starting malonic acids were oxidized by a wet combustion method, and the resulting carbon dioxide collected as barium carbonate.

The C^{14} activity measurements were made using an ionization chamber and a vibrating reed electrometer connected to a Brown recorder. The ionization chambers were filled to a standard pressure with carbon dioxide generated in a vacuum system from the barium carbonate samples with concentrated sulfuric acid. The samples from each run were measured in the same ionization chamber and on the same instrument in as rapid succession as possible in order to minimize any variations in the procedure and instruments. At least two independent activity measurements were made on each sample.

The specific activities of the various samples are shown in Table I. The values given are averages of two or more activity determinations, and the indicated errors are average deviations of these measurements.

The final two columns in Table I show the activity balance between the substituted malonic acid and its decarboxylation products. The activity balance is well within the error of the activity measurements for all of the runs on α-naphthylmalonic acid, and is only 1.1% off in the most widely deviating case with the phenylmalonic acid. The average deviation of the activity balance from 100% is 0.46% for all runs.

Discussion

The decarboxylation of phenylmalonic acid in solution has been shown to be first order with respect to the malonic acid.[15] For malonic acid itself decarboxylation has been shown to be first order, both in the pure liquid and in solution.[16] The kinetics of decarboxylation of several other substituted malonic acids in solution has also been studied,[15,17] and in each case found to be first order in respect to the malonic acid. It therefore seems reasonable to assume that we are dealing with first order reactions here, and if so the specific activities of the products and reactants may be related to the specific rate constants of equations (1), (2) and (3) by the following equations, where

$$\mathrm{HOOCCH(R)COOH} = \mathrm{M} = \mathrm{M}_0 \text{ at } t = 0$$

$$\mathrm{HOOCCH(R)C^{*}OOH} = \mathrm{M}^{*} = \mathrm{M}_0^{*} \text{ at } t = 0$$

$$\mathrm{RCH_2COOH} = \mathrm{A}, \text{ and } \mathrm{RCH_2C^{*}OOH} = \mathrm{A}^{*}$$

$$\frac{\mathrm{C^{*}O_2}}{\mathrm{C^{*}O_2} + \mathrm{CO_2}} = \frac{k_2}{k_2 + k_3}\,\frac{\mathrm{M}_0^{*}(1 - e^{-(k_2+k_3)t})}{\mathrm{M}_0(1 - e^{-k_1 t}) + \mathrm{M}_0^{*}(1 - e^{-(k_2+k)t})} \qquad (4)$$

---

(12) F. F. Blicke and R. F. Feldkamp, *J. Am. Chem. Soc.*, **66**, 1087 (1944).

(13) This basic carbonate cleavage reaction was studied in some detail, and the results are to be published elsewhere.

(14) This procedure was kindly suggested by Professor James Cason.

(15) A. L. Bernoulli and W. Wege, *Helv. Chim. Acta*, **2**, 522 (1919)

(16) (a) C. N. Hinshelwood, *J. Chem. Soc.*, **117**, 156 (1920); (b) J. Laskin, *Tran. Siberian Acad. Agr. Forestry*, **6**, No. 1, 7 (1926); (c) G. A. Hall, Jr., *J. Am. Chem. Soc.*, **71**, 2691 (1949).

(17) A. L. Bernoulli and H. Jakubowicz, *Helv. Chim. Acta*, **4**, 1018 (1921).

TABLE I

SPECIFIC ACTIVITIES OF α-NAPHTHYLMALONIC ACID-1-C^{14}, PHENYLMALONIC ACID-1-C^{14} AND THEIR DECARBOXYLATION PRODUCTS

		Relative specific activity, drift rate, volts/min. × 10^2					
Run No.	Temp., °C.	Carbon dioxide	α-Naphthylacetic acid Observed	× 12[a]	α-Naphthylmalonic acid Observed	× 13[a]	CO_2 + 12 × α-Naphthylacetic acid
Liquid							
1	163.0	1567 ± 3	140.0 ± 1.4	1680 ± 17	250.0 ± 0.3	3250 ± 4	3247
2	163.0	1601 ± 15	144.0 ± 0.4	1728 ± 5	255.4 ± 0.5	3320 ± 6	3329
Solution							
3	100.5[b]	1543 ± 3	141.7 ± 0.1	1700 ± 1	251.0 ± 1.8	3263 ± 23	3243
4	72.8	1561 ± 13	143.0 ± 1.0	1716 ± 12	251.0 ± 2.4	3263 ± 31	3277
5	72.8	1150 ± 1	105.0 ± 0.4	1260 ± 5	184.2 ± 2.0	2395 ± 26	2410
6	87.5	1149 ± 1	104.6 ± 0.0	1255 ± 0	184.3 ± 1.9	2396 ± 25	2404
7	87.5	1543 ± 24	141.2 ± 1.2	1694 ± 14	250.0 ± 2.4	3250 ± 31	3237

Run No.	Temp., °C.	Carbon dioxide	Phenylacetic Acid Observed	× 8[a]	Phenylmalonic acid Observed	× 9[a]	CO_2 + 8 × Phenylacetic acid
Liquid							
1	163.0	1527 ± 9	205.3 ± 0.1	1642 ± 1	368.6 ± 2.0	3173 ± 18	3169
2	163.0	1492 ± 1	205.3 ± 0.0	1642 ± 0	351.4 ± 2.0	3163 ± 18	3134
Solution							
3	72.8	1465 ± 14	209.1 ± 1.1	1673 ± 9	350.2 ± 2.4	3152 ± 22	3138
4	72.8	1468 ± 10	206.1 ± 2.1	1649 ± 17	350.2 ± 2.7	3152 ± 24	3117

[a] Factor to convert to specific activity of the single labeled carbon atom. [b] Bath temperature, actual decomposition temperature unknown, ~85–95°.

$$\frac{A^*}{A^* + A} = \frac{k_3}{k_2 + k_3}\,\frac{M_0^*(1 - e^{-(k_2+k_3)t})}{M_0(1 - e^{-k_1 t}) + M_0^*(1 - e^{-(k_2+k_3)t})} \qquad (5)$$

When the reaction is complete, $t = \infty$, and equations (4) and (5) become, after rearrangement

$$\frac{k_3}{k_2} = \frac{\dfrac{M_0^*}{M_0 + M_0^*} - \dfrac{C^*O}{CO_2 + C^*O_2}}{\dfrac{C^*O_2}{CO_2 + C^*O_2}} \qquad (6)$$

$$\frac{k_3}{k_2} = \frac{\dfrac{A^*_0}{A_0 + A_0^*}}{\dfrac{M_0^*}{M_0 + M_0^*} - \dfrac{A^*}{A_0 + A_0^*}} \qquad (7)$$

By combining equations (4) and (5) *at any time whether the reaction is complete or not*, we obtain equation (8).

$$\frac{k_3}{k_2} = \frac{\dfrac{A^*}{A^* + A}}{\dfrac{C^*O_2}{C^*O_2 + CO_2}} \qquad (8)$$

The values $C^*O_2/(CO_2 + C^*O_2)$, $A^*/(A^* + A)$ and $M_0^*/(M_0^* + M_0)$ are the molar specific activities of the carbon dioxide, the substituted acetic acid and the substituted malonic acid, respectively. These are the values given in Table I.

For ease of tabulation and convenience of reference, the percentage isotope effect may be defined as $100\ (k_3/k_2 - 1)$. The percentage isotope effect values may then be calculated from the data in Table I using equations (6), (7) and (8) with the results shown in Table II. The agreement among the calculations by the three different equations furnishes a measure of the internal consistency of the data. Only two of these three values are independent, however, and the average values and the indicated errors are calculated on the basis of equations (6) and (7) only.

TABLE II

C^{14} ISOTOPE EFFECT IN THE DECARBOXYLATION OF α-NAPHTHYLMALONIC ACID-1-C^{14} AND PHENYLMALONIC ACID-1-C^{14}

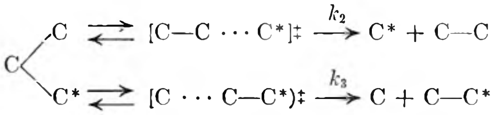
		Per cent. isotope effect, $100(k_3/k_2 - 1)$			
Run No.	Temp., °C.	CO_2 and diacid, equation 6	Monoacid and diacid, equation 7	CO_2 and monoacid, equation 8	Average
		α-Naphthylmalonic acid-1-C^{14}			
Liquid					
1	163.0	7.4	7.0	7.2	7.2 ± 0.2
2	163.0	7.4	8.5	7.9	7.9 ± 0.6
Average	163.0				7.6 ± 0.5
Solution					
3	100.5[a]	11.5	8.8	10.2	10.2 ± 1.3
4	72.8	9.0	10.9	9.9	9.9 ± 0.9
5	72.8	8.3	11.0	9.6	9.6 ± 1.4
Average	72.8				9.8 ± 1.2
6	87.5	8.5	10.0	9.2	9.2 ± 0.7
7	87.5	10.6	8.9	9.8	9.8 ± 0.8
Average	87.5				9.5 ± 0.8
Average all soln. runs					9.7 ± 1.1
		Phenylmalonic acid-1-C^{14}			
Liquid					
1	163.0	7.8	7.3	7.5	7.5 ± 0.3
2	163.0	12.0	8.0	10.1	10.0 ± 2.0
Average	163.0				8.8 ± 1.8
Solution					
3	72.8	15.1	13.2	14.2	14.2 ± 1.0
4	72.8	14.7	9.8	12.3	12.3 ± 2.4
Average	72.8				13.2 ± 1.7

[a] Bath temperature, actual decomposition temperature known, ~85-95°.

The C^{14} isotope effects in the decarboxylation of liquid α-naphthylmalonic acid-1-C^{14} and phenylmalonic acid-1-C^{14} at 163.0° are thus seen to be 7.6 ± 0.5 and 8.8 ± 1.8%. The corresponding values in solution between 72.8 and ~95° are 9.7 ± 1.1 and 13.2 ± 1.7%. The precision of the measurements is not great enough to show a significant temperature coefficient of the isotope effect in the solution experiments. However, there is a significant difference in the isotope effect between the liquid acid at 163.0° and the acid in solution at 72.8 to 95°, and part of this is probably a temperature effect.

These values are in the same range as the other C^{14} work previously mentioned and are much higher than Bigeleisen's calculated *upper limit* of 3.8%.[9]

That these calculations do not represent an actual upper limit may be demonstrated by making similar calculations using a different model from that used by Bigeleisen.[9,18] If we assume that the only vibrations which need be considered in malonic acid are the stretching vibrations of the carbon–carbon bonds, we may picture the reaction in the manner



We may make use of equation (9) as derived by Bigeleisen[19]

$$\frac{k_3}{k_2} = \left(\frac{\mu_2}{\mu_3}\right)^{1/2} \left[1 + \sum_{i}^{3n-6} G(u_i)\Delta u_i \sum_{i}^{3n-7} G(u_i\ddagger)\Delta u_i\ddagger\right] \tag{9}$$

The function G(u) is defined by Bigeleisen and Mayer[20] who have tabulated values of G(u) as a function of u. The reaction coördinate reduced mass, μ, is assumed to be the reduced mass of the atoms forming the bond being broken. The symbol ‡ refers to the activated complex.

In this reaction the term $\sum_{i}^{3n-6} G(u_i)\Delta u_i$ is identically zero since the ground state is the same molecule for the two reactions. In each of the activated complexes, however, one of the carbon–carbon bond force constants is set equal to zero, and as a first approximation, the force constant for the other bond is assumed to be unchanged. In one case this is a C^{12}—C^{12} bond, and in the other case it is a C^{12}—C^{14} bond. Assuming a value of 900 cm.$^{-1}$ for the C^{12}—C^{12} frequency, the C^{12}—C^{14} frequency is calculated as 867 cm.$^{-1}$. If the calculations are carried through using these values, the calculated values for the isotope effect are 7.3% at 80° and 6.2% at 163°. These values are closer to the C^{14} experimental values, but are still not high enough. When the calculation is carried out in this manner for the C^{13} case, the calculated isotope effect is 3.4% at 135°, compared to the experimental values of 2.0 to 2.6%.

If other models are chosen for the activated complex, higher values may be calculated. Applying Pitzer's intermolecular model to the intramolecular case can give values which are too high even for the C^{14} work, and which are a great deal too high for the C^{13} work.

It, therefore, seems pointless to strive for a model which will agree more exactly with the C^{14} work, since it can do so only at the expense of disagreeing with the C^{13} work. Until such time as the apparent discrepancy between the C^{13} and C^{14} experimental results can be resolved, or until a method of calculation can be devised which will agree with both, further calculations serve little purpose.

Another factor which must be considered in determining the over-all isotope effect in a reaction is the possibility of an isotope effect in an equilibrium prior to the rate determining step and multiplying an isotope effect in the latter. Such a situation would be expected to be the rule rather than the exception, since most reactions do involve pre-equilibria of one sort or another. Such an equilibrium in the case of labeled malonic acid might be the equilibrium between the two different hydrogen bonded internal rings. The equilibrium constant for such an equilibrium should be very close to one since there is no change in the number of bonds to the isotopic atom.

Aside from these theoretical calculations, the effect of the substituent on the isotope effect in the decarboxylation of substituted malonic acids is of considerable interest. There is a fairly large difference between the two acids studied in this work, and between them and malonic acid itself, regardless of which value is chosen for the isotope effect in the latter case. It seems possible that resonance stabilization of the incipient intermediate ion in the transition state may have an effect on the isotope effect, in which case we should be able to increase or decrease the effect by appropriate substitution of the aromatic ring.

Experimental

Preparation of Diethyl α-Naphthylmalonate-1-C^{14}.—Diethyl α-naphthylmalonate-1-C^{14} was prepared by the condensation of diethyl oxalate-1,2-C_2^{14} with ethyl α-naphthylacetate according to the procedure of Blicke and Feldkamp.[12] The diethyl oxalate-1,2-C_2^{14} was prepared by esterification of oxalic acid-1,2-C_2^{14}, which was obtained by the reaction of $C^{14}O_2$ with potassium on sand at 360°.

Transesterification of Diethyl α-Naphthylmalonate-1-C^{14}.—A solution of 5.26 g. of diethyl α-naphthylmalonate-1-C^{14} in 25 cc. of glacial acetic acid and 2 cc. of concentrated hydrochloric acid was left standing at room temperature for 1.5 months. At the end of this time the acetic acid, ethyl acetate, water and hydrochloric acid were blown off at room temperature by a stream of air. The yellow crystalline residue was stirred up with benzene and filtered, giving 2.92 g., 69.4% yield, of white prisms of α-naphthylmalonic acid-1-C^{14}, m.p. 156–162° dec. The benzene filtrate contains the unhydrolyzed mono- and diesters along with any α-naphthylacetic acid. The α-naphthylmalonic acid-1-C^{14} was further purified by solution in base, extraction of the solution with ether, decolorization of the basic solution with charcoal, acidification and extraction into ether. Most of the ether was evaporated, the solution was filtered, and a large excess of benzene was added. Upon standing the α-naphthylmalonic acid-1-C^{14} crystallized as fine white prisms, m.p. 162–165° dec. Ivanov and Pshenichnii[21] reported the melting point as "toward 151° dee." The equivalent weight was determined on an inactive sample pre-

---

[18] J. Bigeleisen, *J. Chem. Phys.*, **17**, 345 (1949).

[19] J. Bigeleisen, *ibid.*, **17**, 675 (1949).

[20] J. Bigeleisen and M. G. Mayer, *ibid.*, **15**, 261 (1947).

[21] D. Ivanov and G. Pshenichnii, *Ann. Univ. Sofia, II, Faculte phys.-math. Livre*, [2] **33**, 177–202 (in French, 203–211) 1937); *C. A.*, **32**, 3356^9 (1939).

pared in a similar manner. A sample of 34.3 mg. required 2.97 cc. of 0.1000 *N* sodium hydroxide, giving an equivalent weight of 115.5, calculated, 115.1. Additional recrystallizations of the labeled acid failed to change the melting point (which depended somewhat on the rate of heating) but were carried out in order to ensure complete radioactive purity.

Phenylmalonic acid-1-C^{14}, m.p. 162–165° dec., was prepared in a similar manner from phenylacetic acid and diethyl oxalate-1,2-C_2^{14}.

Decarboxylation Experiments.—The decarboxylation experiments were carried out in an apparatus similar to that previously described.[22]

In a typical experiment, 0.4306 g. of α-naphthylmalonic acid-1-C^{14} was placed in the decarboxylation chamber, a water condenser was affixed using high vacuum silicone stopcock grease to grease the joints, and the system was flushed with dry carbon dioxide-free nitrogen for one hour. The outlet gas was led from the top of the condenser through a spiral trap cooled by a Dry Ice–isopropyl alcohol-bath to remove any solvent or entrained solid, and then through a spiral bubbler. After thorough flushing, the spiral bubbler was filled with carbonate-free 1 *N* sodium hydroxide, and the solvent in the lower flask was heated to reflux, thus heating the decarboxylation chamber to the boiling point of the solvent.

For this experiment the solvent used was mesitylene, giving a decomposition temperature of 163.0°. After a few minutes at 163°, the solid α-naphthylmalonic acid gradually began to melt and simultaneously decarboxylate. The "melting" became progressively faster as more α-naphthylacetic acid "impurity" was formed. Within about 5 minutes of the time the heating was first started all visible reaction had ceased, leaving a clear light yellow liquid. The nitrogen sweep was continued for an additional 1.5 hours to ensure complete recovery of the carbon dioxide. The contents of the sodium hydroxide bubbler were washed into an equal volume of 1 *N* ammonium nitrate, and excess barium chloride was added. The barium carbonate formed, when collected and dried, weighed 0.3708 g., 100.5% yield. The α-naphthylacetic acid-1-C^{14} was washed from the decarboxylation chamber with the aid of alcohol, and was titrated with 1.000 *N* sodium hydroxide, 1.87 cc. being required for neutralization. Assuming complete reaction, this gives a yield of 100.0%. The basic solution from the titration was evaporated to dryness, dissolved in water and extracted with ether. The aqueous phase was acidified, decolorized with charcoal and the hot solution filtered. Upon cooling the α-naphthylacetic acid crystallized out, sometimes in needles and sometimes in plates. The crude acid was recrystallized twice more from boiling water. The final product melted at 128–130°.

In the solution experiments the solid α-naphthylmalonic acid-1-C^{14} was placed in the decarboxylation chamber and dissolved in 3 cc. of dioxane which had been purified by distillation over hydrochloric acid and then over sodium. Nine cc. of 1 *N* hydrochloric acid was added, and the flushing procedure carried out as described above. In this case the gas inlet tube served to stir the solution in the decarboxylation chamber. The solvents used for the constant temperature bath in the solution experiments were technical ethyl acetate, b.p. 72.8°, technical dioxane, b.p. 100.5°, and the dioxane–water azeotrope, b.p. 87.5°, containing 18% water. In these experiments the reaction was considerably slower, and the reactions were allowed to run overnight. Visible bubbles were no longer apparent after about 2 hours, and the initially clear solution had become turbid. A short time later several drops of yellow oil had collected in the bottom of the decarboxylation chamber. Apparently the α-naphthylacetic acid was less soluble than the malonic acid. Blank runs on the procedure, omitting only the α-naphthylmalonic acid, gave only 0.1–0.5 mg. of barium carbonate.

Combustion of α-Naphthylmalonic and α-Naphthylacetic Acids.—Samples of the α-naphthylmalonic acid-1-C^{14} and of the α-naphthylacetic acid-1-C^{14} were oxidized to carbon dioxide by a modified Van Slyke–Folch wet combustion. From 0.1077 g. of α-naphthylmalonic acid-1-C^{14}, 1.2173 g., 101.4% yield, of barium carbonate was obtained, and from 0.1068 g. of α-naphthylacetic acid-1-C^{14}, 1.1516 g., 101.4%, yield was obtained. All the barium carbonate yields reported are high by about 1.2% due to coprecipitated barium hydroxide. This correction was determined by comparing the pressure of carbon dioxide evolved from the barium carbonate samples in a constant volume system with the corresponding pressure from a sample of pure barium carbonate.

---

[22] A. Fry and M. Calvin, THIS JOURNAL, **56**, 897 (1952).

ISOTOPE EFFECT IN SOME REACTIONS OF CARBON-14-LABELED CARBONATOTETRAMMINE COBALTIC COMPLEX ION

By D. R. Stranks and G. M. Harris

Department of Chemistry, University of Melbourne, Melbourne, Australia

Received March 6, 1952

The exchange equilibrium in aqueous solution between carbonatotetrammine cobaltic complex ion and free carbonate ion has been investigated by means of radiocarbon tracer. The equilibrium constant of the reaction, defined as the ratio of equilibrium specific activity of complexed to that of total free carbonate, was 0.875 ± 0.002 at 0°, increasing to 0.900 ± 0.004 at 30°. The apparent heat of reaction was −140 ± 25 cal./mole. The unidirectional acidic decomposition of aqueous solution of labeled carbonato complex, studied by a process of fractional examination of product specific activity, exhibited no significant isotope effect. The results of both the equilibrium and decomposition reaction investigations are satisfactorily interpreted by a qualitative application of statistical mechanical theory.

Carbonatotetrammine cobaltic complex salt (CTC) undergoes a moderately rapid exchange reaction with uncomplexed carbonate in aqueous solution.[1] A preliminary study[2] has indicated that the equilibrium distribution of radiocarbon tracer among the exchanging species is appreciably nonstatistical. The present paper describes a more detailed examination of this isotope effect, including its temperature dependence. In addition, the ratio of the rates of acidic decomposition in aqueous solution of labeled and unlabeled CTC were determined. These related researches provide, for a single carbon-14-labeled compound, investigations of two of the types of chemical process in which isotope effects have been previously observed—exchange equilibration[3] and unidirectional decomposition.[4]

The equilibrium under consideration may be regarded as being made up of either one or both of two possible over-all exchange systems

$$Co(NH_3)_4CO_3^+ + HC^*O_3^- \rightleftarrows Co(NH_3)_4C^*O_3^+ + HCO_3^-$$

or

$$CO(NH_3)_4CO_3^+ + C^*O_3^= \rightleftarrows Co(NH_3)_4C^*O_3^+ + CO_3^=$$

The first of these singly is supported by the kinetic investigation mentioned.[1] However, the equilibrium constant of the system

$$CO_3^= + HC^*O_3^- \rightleftarrows C^*O_3^= + HCO_3^-$$

has almost certainly a value of approximately unity in the neighborhood of room temperature.[5] It is therefore of no great importance whether the complex ion/carbonate exchange is considered in terms of $CO_3^=$ or HCO_3^- ions. In any case, the practical equilibrium constant

$$K = \frac{[Co(NH_3)_4C^*O_3^+][HCO_3^- + CO_3^=]}{[Co(NH_3)_4CO_3^+][HC^*O_3^- + C^*O_3^=]} \quad (1)$$

is a straightforward definition of isotopic enrichment effects in this system. Given in terms of specific radioactivities of carbon-14 tracer, K is simply the ratio of the equilibrium specific activity of CTC to that of total uncomplexed carbonate.

The unidirectional decomposition of an isotopically labeled compound to give products, only one of which is to contain labeling atom, may be represented

$$A + B + \ldots \xrightarrow{k} P + Q + \ldots$$
$$A^* + B + \ldots \xrightarrow{k^*} P^* + Q + \ldots$$

With label present in tracer concentration only, the relative rates of formation of product molecules P* and P is given by

$$\frac{d[P^*]}{d[P]} = \frac{k^*[A^*]}{k[A]}$$

irrespective of the reaction mechanism.[6] Proceeding in a manner analogous to the treatment of the case of fractional examination of reactant,[7] it is readily shown that

$$\frac{d[P^*]_\gamma}{d[P]_\gamma} = \frac{[A^*]_0}{[A]_0}\,\epsilon(1 - \gamma)^{\epsilon-1}$$

In this, ϵ is the rate constant ratio k^*/k, and the subscripts 0 and γ refer to concentrations initially and at fraction of reaction γ, respectively. In terms of specific radioactivities, the expression above is closely approximated up to a high fraction of reaction by

$$S\gamma/S_0 = \epsilon(1 - \gamma)^{\epsilon-1} \quad (2)$$

Here, $S\gamma$ represents specific activity of small *product* increment collected over interval of reaction of average fraction γ, and S_0 is the initial specific activity of *reactant.* The form of this function is such that small divergences of ϵ from unity are considerably magnified during the last stages of reaction.[8]

---

(1) G. M. Harris, *J. Chem. Phys.*, **18**, 764 (1950); G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952).

(2) D. R. Stranks and G. M. Harris, *J. Chem. Phys.*, **19**, 257 (1951).

(3) H. C. Urey, *J. Chem. Soc.*, 562 (1947), gives a full review of stable isotope exchange work, including C^{12}/C^{13} systems. Nothing other than reference (2) above has yet been published on isotope effects in C^{12}/C^{14} exchange equilibria.

(4) Carbon-14 effects in such reactions have been reported by the following: Albert L. Myerson and F. Daniels, *Science*, **108**, 676 (1948); P. E. Yankwich and M. Calvin, *J. Chem. Phys.*, **17**, 109 (1949); J. W. Weigl and M. Calvin, *ibid.*, **17**, 210 (1949); W. H. Stevens and R. W. Attree, *Can. J. Res.*, **B27**, 807 (1949); *J. Chem. Phys.*, **18**, 574 (1950); W. O. Armstrong, Leon Singer, S. H. Zbarsky and B. Dunshee, *Science*, **112**, 531 (1950); A. Roe and M. Hellmann, *J. Chem. Phys.*, **19**, 660 (1951); E. A. Evans and J. L. Huston, *ibid.*, **19**, 1214 (1951).

(5) Experimental data reported in reference (3) suggest a value of very close to unity for the constant as applied to a C^{13}/C^{12} system. Statistical mechanical calculations to be discussed below lead to a figure of 0.982 for the corresponding C^{14}/C^{12} constant at 293°, with a very slight temperature coefficient.

(6) Let the over-all rate law be of the form $k[A]^m[B]^n\ldots$ With only tracer concentration of labeled reactant A*, the corresponding rate law governing formation of P* will be of the form $k^*[A^*][A]^{m-1}[B]^n\ldots$, since the probability of molecules A* participating more than once in the mechanism is negligible.

(7) A. M. Downes and G. M. Harris, *J. Chem. Phys.*, **20**, 196 (1952).

(8) For example, with $\epsilon = 0.9$, the increment of product taken between $\gamma = 0.85$ and $\gamma = 0.90$ will have an average $S\gamma$ value about 21% greater than its initial value. For the $\gamma = 0.90$ to $\gamma = 0.95$ increment, the corresponding figure is 30%.

It is clear that fractional examination of product specific activity should enable detection of any appreciable isotope effect, notwithstanding the unavoidable experimental uncertainty in such activity determinations.

Referring specifically to the acid decomposition of CTC in aqueous solution, the over-all reaction is known to be[9]

$$Co(NH_3)_4CO_3^+ + 2H^+ + H_2O \longrightarrow Co(NH_3)_4(H_2O)_2^{+++} + CO_2$$

One can make successive additions of small portions of strong mineral acid to tracer-labeled complex salt, and determine the relative activities of the series of carbon dioxide samples evolved. A reasonable approximation to the relevant ϵ factor should then be attainable by application of equation (2).

Experimental

A. **The Exchange Equilibrium.**—CTC nitrate and carbon-14-labeled sodium carbonate were prepared as previously described.[1] Aqueous solutions of the reactants were equilibrated at constant temperature (± 0.01°) for a minimum of seven half-times of exchange (*i.e.*, to within 0.78% of complete equilibrium). The required half-times for various conditions of reactant concentration, *p*H, ionic strength, and temperature were known from the previous kinetics work.[1] After equilibration, uncomplexed carbonate was precipitated as barium carbonate, mounted, and assayed for radioactivity exactly as described in the earlier study. Assay of the filtrate containing the CTC was effected by means of a semi-micro modification of a standard closed-system technique of carbonate determination.[10] A typical experiment proceeded as follows. After evacuation of the apparatus to water pressure, 6 *N* CO_2-free hydrochloric acid (2 ml.) was run from an attached funnel into a portion of CTC solution (0.2 ml. in 4 ml. CO_2-free water) contained in the main reaction vessel. When evolution of gas had ceased, the acidified solution was boiled by immersion in an oil-bath, steam and CO_2 being driven over into a cool sidearm containing 0.5 *N* sodium hydroxide (1 ml.). Ten-minute cooling periods were alternated with the boiling operation.

Test experiments showed that carbonate recovery was complete after the third repetition of the boiling-cooling routine. CO_2-free air was then admitted, and the carbonate solution transferred with washings to a centrifuge tube. Barium carbonate samples were prepared essentially as before, except that in order to obtain precipitates amenable to spreading much slower addition of precipitating reagent was necessary than in the case of less alkaline carbonate solutions. Despite all precautions, occasional samples were obviously badly spread and were discarded. Moreover, any samples the mass of which differed by more than 0.2 mg. from the mean mass (about 3 mg. usually) of a series of identical samplings were also rejected. All counts were done with a conventional thin-end-window G–M tube and accessories. They were sufficiently prolonged to reduce the random standard deviation to within 0.5%, and were repeatedly checked.

B. **The Acidic Decomposition.**—Carbon-14-labeled complex salt was prepared by equilibration of inactive CTC in solution with radioactive uncomplexed carbonate. After 13 hours reaction at 25° (about 4 half-times) the solution was cooled to 0°, and ice-cold absolute alcohol was added. The precipitated active CTC nitrate was filtered off on a sintered-glass funnel, thoroughly washed in ice-cold alcohol, and dried *in vacuo* over anhydrous silica gel. The final product, recovered in 83% yield, contained no detectable free carbonate ion. The step-wise acid decomposition of labeled CTC was accomplished by means of the apparatus illustrated in Fig. 1.

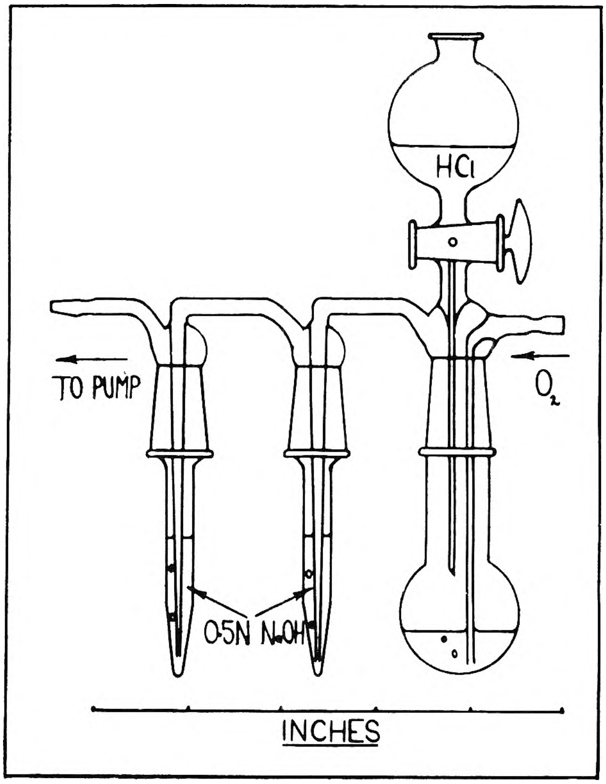


Fig. 1.—Acidic decomposition apparatus.

CO_2-free hydrochloric acid (0.2006 *N*) was added in accurately measured aliquots from the small funnel to the 8-ml. capacity decomposition flask containing solution of a known weight of active CTC nitrate in 2 ml. of CO_2-free water. The volume of acid aliquot for each fraction of decomposition was determined by addition of a definite number of drops of known average volume. Tests showed that this procedure was very accurate when the rate of drop addition was carefully standardized. Decomposition of CTC was known from *p*H measurements to go to near completion very rapidly. For example, at 25°, the temperature of the experiments, the *p*H rose from an initial value of *ca.* 2.2 immediately on addition of the acid to 4.2 in 30 seconds, after which only a slight further rise slowly occurred. Temperature control of the reaction vessel to within ± 0.02° was maintained by immersion of the spring-held decomposition flask in a small thermostat.

The CO_2 produced (about 0.015 millimole per fraction of decomposition) was entrained in purified oxygen bubbled through the reaction mixture.[11] Sweeping was continued for five minutes after addition of acid, the CO_2–O_2 mixture bubbling through CO_2-free sodium hydroxide (0.5 ml. of 0.5 *N* solution) contained in the 1.5-ml. capacity tapered absorption tubes. The resultant carbonate solutions were transferred to a centrifuge tube by dropper pipet, together with two washings of the absorption tubes and bubbler capillaries. Preparation of the barium carbonate plates and their counting was carried out as already indicated. Preliminary tests showed that quantitative recovery of carbonate radioactivity was achieved by the procedure outlined. However, despite rigorous purification of reagents and careful attention to details of technique, a small blank of inactive carbonate could not be eliminated. By standardization of the routine, especially as regards timing, it was found possible to make the blank consistently reproducible at 0.265 ± 0.005 mg. of barium carbonate per sample. With this constant blank, all radioactive assay results were readily expressed on a common standard of comparison.

Results

A series of exploratory experiments was first carried out at 20.3° to detect possible major dependences of the exchange equilibrium constant on conditions such as *p*H, reactant ratio, ionic strength, light intensity, and surface of container. The results are recorded in Table I. It is obvious

---

[9] Abegg, "Handbuch der anorganischen Chemie," Hirzel, Leipzig, 1935; Bd. IV, Abt. 3, Teil 3, p. 771.

[10] H. T. S. Britton, "Hydrogen Ions," Vol. II, Chapman and Hall, London, 1942, p. 174.

[11] Boiling could not be employed here to drive off the gas since thermal decomposition of the residual CTC would also take place.

TABLE I

EFFECT OF CONDITIONS OTHER THAN TEMPERATURE ON EXCHANGE EQUILIBRIUM CONSTANT

Expt. No.	Concn. CTC (mole/l.)	Concn. $CO_3 + HCO_3$ (mole/l.)	No. of detn.	Mean K for Expt.	Remarks
1	0.03376	0.01469	2	0.886	*p*H *ca.* 10
2	.03376	.01469	2	.892	*p*H *ca.* 9
3	.05746	.01460	2	.894	*p*H 9.47
4	.03710	.01604	2	.890	*p*H 9.7, μ = 0.0799 (adjusted by addition of $NaNO_3$)
5	.03710	.01604	3	.893	*p*H 9.7, μ = 0.4000
6	.03379	.01471	1	.887	Exchanged in absence of light.
7	.03379	.01471	1	.895	Exchanged under illumination by adjacent 15w. tungsten light
8	.03389	.01470	1	.891	Reaction vessel packed with glass granules
			14	0.891	±0.002 weighted mean K and its standard deviation

TABLE II

TYPICAL SERIES OF K DETERMINATIONS AT 273.2° A.

(Applies to Table III also): m_α, m_β = mass of $BaCO_3$ samples from free carbonate and from CTC, respectively; A_α, A_β = activities (ct./mg. $BaCO_3$/min.) of free carbonate and CTC samples; γ = [CTC]/[free carbonate] = 3.936

Detn No.	m_α, mg.	m_β, mg.	A_α	A_β	γA_β	$A_\alpha + \gamma A_\beta$	$K = A_\beta/A_\alpha$
1	2.74	2.81	224	196	772	996	0.875
2	2.68	2.68	226	194	764	990	.858
3	2.76	2.67	224	195	768	992	.871
4	2.72	2.82	224	198	779	1003	.884
5	2.73	2.77	225	196	772	997	.871
6	2.70	2.72	226	197	775	1001	.872
7	2.76	2.80	223	196	772	995	.879
8	2.71	2.70	222	196	772	994	.883
		Mean	224.3	196.0	771.6	996.0	.874
		S.D. of Mean	± 0.49	± 0.42	± 1.65	± 1.72	± .003
	Initial activity (check only —mean of 2 detn.)		996	....	....	996	

TABLE III

TEMPERATURE DEPENDENCE OF EXCHANGE EQUILIBRIUM CONSTANT

Expt. No.	Temp. (°A.)	No. of detn.	Mean A_α	Mean A_β	$A_\beta + \gamma A_\beta$	Initial specific activity of free carbonate (check only)	Mean K and its S.D.
1	273.2	8	224.3	196.0	996.0	996	0.875 ± 0.002
2	273.2	8	224.1	196.1	996.1	998	
3	288.2	8	220.0	194.0	983.7	992	.882 ± .003
4	293.5	6	210.8	187.5	948.7	954	.891 ± .005
5	298.2	8	211.0	188.2	951.8	962	.894 ± .002
6	298.2	8	205.7	184.3	931.1	935	
7	303.2	8	213.8	192.5	971.5	980	.900 ± .004

that K is constant to well within ± 1% of 0.89 at this temperature, regardless of the other variables.

A more extensive series of determinations was then undertaken over the temperature range 0–30°, other conditions being fixed as follows: *p*H 9.47; concentration of CTC = 0.05746 mole/l.; concentration of free carbonate = 0.01460 mole/l. Higher temperature studies were not attempted because of the observable thermal decomposition of CTC in aqueous solution above 20°. (On long standing, a brownish opalescence due to cobaltic oxide precipitation appears.) In order to eliminate this complication in the experiments at 25 and 30°, the solutions were first equilibrated at 0° (a minimum of seven half-times of exchange), then maintained at the higher temperature for about three additional half-times. This procedure can be shown to have brought each system finally to within the experimental error in the determination of the true higher temperature equilibrium condition.

A total of 54 independent determinations of K was made. The nature of the results obtained is illustrated in detail for one series of measurements at 0° in Table II. Table III summarizes the data for all experiments, together with the mean K value and its statistical standard deviation, at each temperature. A least squares analysis was performed on the assumption of the linear relationship: $\log K = -\Delta H/2.303RT + \text{constant}$. Each of the 54 K values was treated individually and of equal weight. The value of ΔH, the apparent heat of reaction, so obtained was −140 cal./mole. with a statistical standard deviation of ± 25 cal./mole.

The fractional acidic decomposition data are summarized in Table IV. Individual masses of the barium carbonate

TABLE IV

FRACTIONAL ACIDIC DECOMPOSITION OF LABELED CTC SALT

Expt. No.	No. Fractions taken	Specific activities of individual fractions (Counts/mg. $BaCO_3$/min.)	Mean activity and its std. deviation	Total mass of samples Recov., mg.	Total mass of samples Calcd., mg.
1	10	770, 730, 774, 798, 765 802, 803, 826, 779, ...[a]	783 ± 9.3	32.13	32.44
2	11	796, 801, 801, 785, 792, 796 789, 800, 807, 818, 796	798 ± 2.7	31.05	32.44
4	10	781, 819, 781, 796, 795 765, 792, 784, ...,[a] 786	789 ± 4.8	31.36	32.48
5	21	796, 770, 789, 796, 812, 783, 786, 788, 798, 789, 795, 820, 822, 808, 814, 801, 801, 796, 804, 785, 783	797 ± 2.9	64.08	64 88
3	..[b]	780, 785, 802, 798, 795, 800	795 ± 3.6	19.23	19.46

[a] Sample spoiled accidentally. [b] Samples prepared by complete decomposition of equal portions of labeled complex in order to give independent estimate on S_0 value.

samples (all close to 3 mg.) are not recorded. However, the total recovered mass for each series of determinations is seen to agree well with that predicted by calculation from the known quantity of CTC salt taken and the known standard blank. Inspection of the figures does not suggest any obvious trend in the activity values as reaction proceeds. This observation is confirmed by detailed least squares analysis of all individual activities, treated in terms of equation (2) in the form

$$\log S_\gamma = \log S_{0\epsilon} + (\epsilon - 1) \log (1 - \gamma)$$

No appreciable deviation of ϵ from unity was indicated,[12] from which it may be concluded that the over-all isotope effect operative in this decomposition process is very slight.

Discussion

The equilibrium constant of the system, as has been shown above, can be defined in either of two ways. In terms of partition function ratios, the expressions are

$$K_1 = f_{\mathrm{CTC}}/f_{\mathrm{HCO_3}} \quad \text{or} \quad K_2 = f_{\mathrm{CTC}}/f_{\mathrm{CO_3}}$$

the f's being the ratios of the functions for carbon-14-labeled and normal entities, respectively, ($f = Q_{14}/Q_{12}$). The molecular structure data available on such a complicated substance as CTC ion are, of course, inadequate for any direct estimation of the magnitude of its partition function. Nevertheless, by postulating probable structural modifications of a carbonate ion on becoming complexed, a reasonable qualitative interpretation of the observed results is possible.

In the CTC ion, two of the carbonate oxygen atoms are covalently attached to the central cobaltic ion.[13] This binding modifies the symmetrical XY_3 form of the free carbonate ion to what is in effect an XYZ_2-type of structure. Moreover, the two bonds between the coördinating oxygens and carbon are weakened on complex formation, and the effective mass of these oxygens is increased (say by one-sixth of the cobaltic ion mass). Vibrational modes of the CTC ion not directly associated with its constituent carbon atom will be but slightly affected by the isotopic substitution, so may be neglected in the evaluation of f_{CTC}. A reasonable estimate, therefore, of the order of magnitude of f_{CTC} should be given by evaluating the corresponding function for a molecule approximating to the postulated form of the complexed carbonate ion. Such a molecule is phosgene, $COCl_2$.

The partition function ratios required for the determination of K_1 and K_2 according to the scheme just outlined have been calculated. The procedure was analogous to that of Urey[3] for C^{13}/C^{12} systems. Table V records the data relevant to the present discussion, including figures for $f_{\mathrm{CO_2}}$ and a constant K_3 to be referred to later. The details of the calculations, together with the results obtained for a number of other possible C^{14}/C^{12} exchange systems, will be published separately.[14] It is seen that the earlier assumption of near equivalence of HCO_3^- and CO_3^- in the exchange system is justified, since both predicted K's are in good qualitative agreement with the experimental finding (see Table III). The ΔH values, calculated from the K_1 and K_2 data according to the conventional isochore treatment, are −115 and −104 cal./mole, respectively, again reasonably consistent with the observed ΔH(−140 ± 25 cal./mole).

TABLE V

PARTITION FUNCTION RATIOS FOR VARIOUS MOLECULES

Temp., °A.	$f_{\mathrm{HCO_3^-}}$	$f_{\mathrm{CO_3^-}}$	$f_{\mathrm{CO_2}}$	$f_{\mathrm{COCl_2}} = f_{\mathrm{CTC}}$	K_1	K_2	K_3
273.16	1.5085	1.4784	1.4444	1.2948	0.858	0.876	1.116
293.16	1.4507	1.4239	1.3973	1.2634	.871	.887	1.106
313.16	1.4025	1.3784	1.3580	1.2370	.882	.897	1.098

In order to consider the acidic decomposition reaction, the first requirement is to assign it a definite mechanism. That suggested by the previously published exchange kinetics study[1] is

$$\mathrm{Co(NH_3)_4CO_3^+ + H_3O^+ \xrightarrow{k_1} Co(NH_3)_4HCO_3{\cdot}H_2O^{++}}$$

$$\mathrm{Co(NH_3)_4HCO_3.H_2O^{++} + H_3O^+ \xrightarrow{k_2} Co(NH_3)_4(H_2O)_2^{+++} + H_2O + CO_2}$$

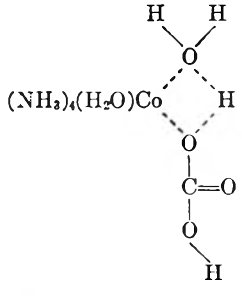
with the second reaction rate-determining.[15]

On the basis of the statistical mechanical theory of isotope effects in unidirectional reactions[16] the rate constant ratio required for the present system is given by

$$k_2^*/k_2 = f_{\mathrm{A}}/f_{\mathrm{B}}\left(\frac{m}{m^*}\right)^{1/2} \tag{3}$$

This assumes equality of transmission coefficients for labeled and unlabeled reactant. The symbols f_{A} and f_{B} are the partition function ratios as defined above for activated complex and bicarbonatoaquotetrammine cobaltic ion, respectively.

The quantities m are defined as the reduced mass of the atoms forming the bond broken in the reaction,[17] in each instance here a cobalt–oxygen bond. The ratio m/m^* will thus have a value unity. The activated complex may be visualized as



Clearly, the vibrational characteristics of the coördinated bicarbonate ion should not be greatly modified by the activation process. It is therefore reasonable to expect that f_{A} and f_{B} will not differ greatly in magnitude, if at all. Consequently, k_2^*/k_2 should have a value close to unity, as is found experimentally.

A similar argument to that just given can be applied with a similar result if k_1 is assumed to be rate-determining rather than k_2. With other possible

---

[12] The actual figures obtained were $S_{0\epsilon}$ = 790.2 ± 1.4 and (ϵ − 1) = −0.004 ± 0.0014, leading to ϵ estimates of 0.994 ± 0.0048 and 0.996 ± 0.0014, respectively.

[13] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, Chapt. III.

[14] D. R. Stranks and G. M. Harris, to be published.

[15] In view of the rapidity with which the carbon dioxide is formed and removed from the system (see Experimental) it is deemed unnecessary in the present instance to consider possible isotopic exchange complications involving the reverse reactions.

[16] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[17] N. B. Slater, *Proc. Roy. Soc.* (*London*), **194**, 112 (1948).

mechanisms of the reaction, however, the expectation is otherwise. For example, if the activated complex relevant to k_2 is conceived as a simple dissociated entity $Co(NH_3)_4H_2O^{+++}$, HCO^-_3, f_A would be equivalent to f_{HCO_3}. This would predict for k_2^*/k_2 a value of the order of magnitude of $1/K_1$, since f_B should not differ greatly from f_{CTC}. Alternatively, it might be assumed that, on addition of acid, complete equilibrium is established prior to removal of the carbon dioxide fraction, as

$$Co(NH_3)_4CO_3{}^+ + 2H^+ + H_2O \rightleftarrows Co(NH_3)_4(H_2O)_2{}^{+++} + CO_2$$

The portion of gas removed at fraction of reaction γ would then have its isotopic composition defined by

$$\frac{[C^{14}O_2]_\gamma}{[CO_2]_\gamma} = K_3 \frac{[Co(NH_3)_4C^{14}O_3{}^+]_\gamma}{[Co(NH_3)_4CO_3{}^+]_\gamma} \qquad (4)$$

K_3 is the ratio of the equilibrium constants of the reaction above with reference to labeled and unlabeled reactants, respectively. It is readily seen to have the magnitude $K_3 = f_{CO_2}/f_{CTC}$, the predicted values for which are given in Table V. It is clear from the form of equation (4) that these figures lead to a result contrary to observation. One can safely conclude that neither of the mechanisms last discussed can be operative in this reaction.

DISCUSSION

J. P. Hunt (University of Chicago).—The experiments of Hunt, Rutenberg and Taube (*J. Am. Chem. Soc.*, **74**, 268 (1952)) on aquation of $Co(NH_3)_5(CO_3)^+$ show that here the C–O bond is broken rather than the Co–O bond. It is suggested that such would also be the case for the aquation of $Co(NH_3)_4(H_2O)(HCO_3)^{++}$. One would ask whether or not this affects the argument involving the isotope effect. If the exchange

$$H_2O^{18} + Co(H_2O)_6{}^{3+} \rightleftarrows Co(H_2O)_5(H_2O^{18}) + H_2O$$

was rapid, one might conclude that the Co–O bonds are broken relatively easily in this system. The experiments at present do not distinguish between rapid water exchange and catalysis by Co^{+2} aq. due to electron transfer.

J. Bigeleisen.—In the paper which I presented on Wednesday morning, I called attention to some work by Dr. Lewis Friedman and myself (*J. Chem. Phys.*, **18**, 1325 (1950)) on the isotope effects in the decomposition of ammonium nitrate. It was established in this work that there are some bonds in the transition state which are stronger than in the normal molecule. A similar situation exists in the thermal deammonation of phthalamide (*Canadian Journal of Chemistry*, **30**, 443 (1952)). If a similar situation exists in the acid decomposition of the carbonatotetrammine cobaltic ion, there would be no conflict with the absence of an isotope effect measured by Stranks and Harris and the possibility that the C–O bond breaks.

G. M. Harris.—One can also get around the difficulty by accepting the alternative mechanism, in which k_1 is assumed to be rate-determining, though this would require re-interpretation of the exchange kinetics data (Harris and Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952)).

Peter E. Yankwich (University of Illinois).—Dr. John McNamara and I have measured the equilibrium constant for C^{13} and C^{14} exchange and the corresponding relative rates in the reaction, involving the carbonato-bisethylenediamine cobalt(III) ion, a system similar to that studied by Stranks and Harris. We found for K, as defined by their equation (1), $0.99_0 \pm 0.01_5$ for C^{14} and $0.99_1 \pm 0.01_3$ for C^{13}; C^{13} exchanged $1.03_3 \pm 0.02_8$ times as rapidly as C^{14}. A double check of K for C^{13}, in which a technique independent of blank corrections was employed, gave the value $1.000_4 \pm 0.000_4$. One could predict from the "missing" isotope effects in this system that exchange would be more rapid than in the carbonato-tetrammine system. Our kinetic data could be compared with that reported recently by Stranks and Harris, in the *Transactions of the Faraday Society*, only at two points; at both these points the exchange in the bis-ethylene system is somewhat the more rapid.

J. Bigeleisen (Brookhaven Nat. Lab.).—The assumptions made by Stranks and Harris in the calculation of the partition function ratios, "f" values, are such that it is improper to list their deviation from unity to four significant figures. I believe that three significant figures are all that are justified and in some instances just two. It is rather interesting that in the equilibrium experiments the C^{14} concentrates in the $CO_3^=$. This means that the bonding of the carbon to oxygen in carbon is appreciably weakened in the formation of the complex, possibly as a result of destruction of resonance in the carbonate ion.

G. M. Harris.—This is the implication of our assumption that the complexed carbonate ion has properties more similar to $COCl_2$ than to CO_3. In regard to the system studied by McNamara, it would appear that in the bis-ethylenediamine complex the carbonate ligand is much less modified than in the tetrammine. Such a difference is not inconceivable, in view of the known considerable differences in the chemistry of these two substances.

EFFECT OF ISOTOPIC SUBSTITUTION ON THE COLLISION PROPERTIES OF THE CARBON DIOXIDE MOLECULE

By E. W. Becker and W. Beyrich

Physics Institute, University of Marburg, Marburg/Lahn, Germany

Received March 6, 1952

For quantum mechanical reasons symmetric and unsymmetric isotopic substitutions are expected to have different effects on the collision properties and reaction rates of molecules. Therefore the collision properties of symmetrically and unsymmetrically substituted CO_2 molecules have been investigated by means of the thermal diffusion method. A difference of 78° was found between the thermal diffusion reversing temperatures of the pairs $O^{16}C^{13}O^{16}/O^{16}C^{12}O^{16}$ and $O^{16}C^{12}O^{17}/O^{16}C^{12}O^{16}$, the partners of the common $O^{16}C^{12}O^{16}$ being equal in mass but different in symmetry. The difference cannot be explained on a classical basis and may be due to the quantum mechanical symmetry effect expected from theory. At any rate the experiments show that the collision properties of a molecule can jump with an isotopic substitution, the change in these properties being nearly independent of the relative change in mass. A further experiment is suggested to decide whether nuclear isomers are identical particles in the quantum mechanical sense.

Introduction

The change of the *chemical potential* of a compound with the introduction of an isotope results, on the one hand, from the influence of the masses on the characteristic frequencies and moments of inertia of the molecules, and on the other hand from a change of their symmetry number.[1] While the first effect is a function of the relative mass difference the second is based on the quantum mechanical *non-identity* of the isotopes. The influence of the symmetry number on the chemical potential vanishes with a high order of the ratio Θ/T (Θ = characteristic rotational temperature, T = absolute temperature) and is, at room temperature, of practical importance only for the hydrogen isotopes.

The isotopic effect on the *reaction rate*, however, may be influenced by a change in symmetry number even with the heavier elements: For example the molecule $O^{16}C^{12}O^{16}$ having the symmetry number 2 can rotate only in every second state. If one of the two O^{16} is substituted by O^{18} the molecule can rotate in every state, since the symmetry number has been reduced to 1. In a collision a molecule of symmetry number 2 can change its rotational state only by two levels, while with a molecule of symmetry number 1 a transition into a neighboring state is possible. Therefore the collision properties of a molecule, and in connection with them the reaction properties, may depend on the symmetry number. The substitution of one of the O^{16} in a CO_2 molecule by O^{18} as well as by O^{17} should have the same effect on the collision properties, while the substitution of the carbon atom should have no effect of this kind,[2] since in this case the symmetry number remains unaffected.

An experimental proof of these expectations is possible by comparing reaction rates of molecules having different symmetry. Owing to experimental difficulties, however, we started to investigate the collision properties of symmetric and unsymmetric molecules using the *thermal diffusion* method.

Ordinarily thermal diffusion is understood as the partial separation of gases *having different molecular weights*, which takes place in a temperature gradient. As is well known this effect can be multiplied in the Clusius–Dickel column[3] and can be used to enrich rare isotopes. Furthermore thermal diffusion occurs with gases of *equal* molecular weight having *different intermolecular forces*, hence they will have different effective diameters.[4] Therefore the collision properties depending on the *symmetry number* are expected to show up in thermal diffusion, too. Thus in a mixture of gases thermal diffusion should occur even with components which are equal in mass and intermolecular forces but different in symmetry number. A mixture of $O^{16}C^{13}O^{16}$ and $O^{16}C^{12}O^{17}$ therefore should be separable in a thermal diffusion column.

Since a pure mixture of these components was not available, the experiments were carried out with natural CO_2, the composition of which is given in Table I. At first sight the conditions in natural CO_2 seems to be hopelessly complicated by the great number of different molecular species. Actually the problem is much simpler since all components practically collide only with $O^{16}C^{12}O^{16}$ being by far the most abundant. This fact will be essential in the evaluation of our experiments.

Experimental

A separation column, 10 m. in length, was filled with CO_2 at 5.5 atm. The inner and outer diameters of the concentric tubes were 13.0 and 16.0 mm., respectively. The corresponding temperatures were 117 and 65°. In intervals of about 200 hours samples were taken at the upper and lower end of the separator. The concentration ratios of masses 45 and 44, (V^{45}_{44}), as well as 46 and 44, (V^{46}_{44}), were determined in a mass spectrometer. The enrichment factors

$$A^{45}_{44} = \frac{(V^{45}_{44})\text{ lower end}}{(V^{45}_{44})\text{ upper end}}$$

and

$$A^{46}_{44} = \frac{(V^{46}_{44})\text{ lower end}}{(V^{46}_{44})\text{ upper end}}$$

are plotted against time in part a of Fig. 1. It is surprising that mass 46 is enriched at the upper end, while the concentration of mass 45 is higher at the lower end. Thus *the thermal diffusion factors α of 45/44 and 46/44 have different sign at the chosen mean temperature.*[5]

---

(1) See, *e. g.*, L. S. Kassel, *Chem. Revs.*, **18**, 277 (1936); J. Bigeleisen and M. Goeppert-Mayer, *J. Chem. Phys.*, **16**, 261 (1947); H. C. Urey, *J. Chem. Soc.*, 562 (1947).

(2) Here we take no interest in the simple effect of *mass* on the reaction rate of a molecule.

(3) K. Clusius and G. Dickel, *Z. physik. Chem.*, [b] **44**, 397/473 (1939).

(4) F. T. Wall and C. E. Holley, Jr., *J. Chem. Phys.*, **8**, 949 (1940); K. Clusius and H. Kowalski, *Z. Elektrochem.*, **47**, 819 (1941).

(5) See the preliminary report: E. W. Becker and E. Dörnenburg, *Naturwissenschaften*, **37**, 166 (1950).

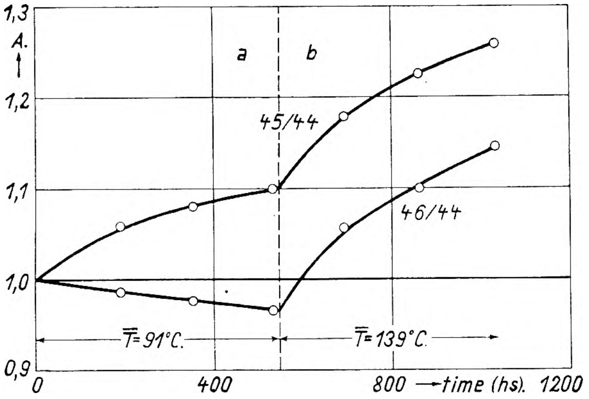


Fig. 1.—Enrichment factors A^{45}_{44} and A^{46}_{44} of run 4 and run 6 (see Table II) plotted against time.

It is not surprising, that a negative thermal diffusion of CO_2 occurs at all, since it is well known from the temperature dependence of the viscosity that the CO_2 molecule is very "soft" in the temperature range under consideration. A similar behavior is known of ammonia.[6] Remarkable, however, is the fact that two different combinations of chemically equal molecules being different in their masses, can have thermal diffusion of different sign, *i.e.*, different mean temperatures at which the sign of thermal diffusion is reversed. It is shown by part b of Fig. 2, taken at $\bar{T}$ = 139°, that the thermal diffusion factor α is positive at that temperature for *both* combinations, the absolute value of α (46/44) however, being smaller than that of α (45/44).[7]

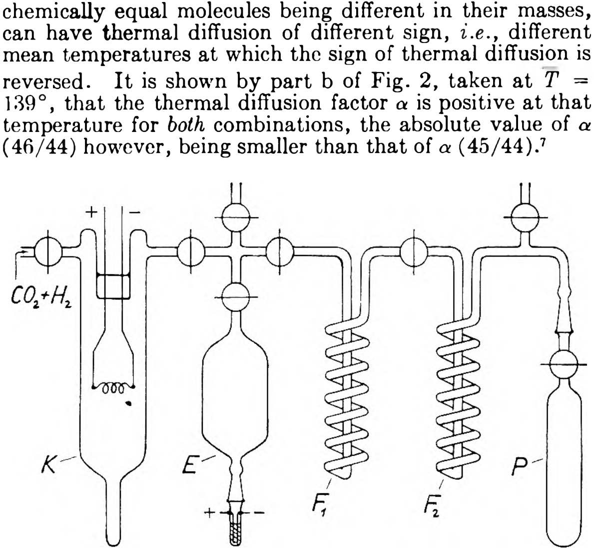


Fig. 2.—Apparatus for converting CO_2 into O_2.

According to the known theories of thermal diffusion a mass dependence of the reversing temperature is not to be expected.[8] This suggested the conclusion that the different behavior of the combinations 45/44 and 46/44 results from the symmetry effect discussed in the introduction: According to Table I mass 46 is represented practically only by the *unsymmetric* molecule $O^{16}C^{12}O^{18}$ whereas mass 45 contains the *symmetric* molecule $O^{16}C^{13}O^{16}$ to an extent of 93%.

In order to exclude an appreciable influence of the molecular masses on the reversing temperature *experimentally*—if it should exist at all in contradiction to the theory—the behavior of the unsymmetric molecule $O^{16}C^{12}O^{17}$, being present in mass 45 to an amount of 7%, had to be investigated. For this purpose oxygen chemically obtained from the CO_2 samples was tested in a mass spectrometer for its O^{17} content.

TABLE I

THE RELATIVE ABUNDANCE OF THE MOST IMPORTANT COMPONENTS OF NATURAL CO_2

(Mass numbers of the atoms in sequence OCO)

Mass	44	45	46	47	48
Relative abundance	(16, 12, 16) 98.4%	(16, 13, 16) 1.12% (16, 12, 17) 0.08%	(16, 12, 18) 0.40% (16, 13, 17) 0.0009%	(16, 13, 18) 0.005% (17, 12, 18) 0.0002%	(18, 12, 18) 0.0004%

The preparation of the oxygen was done with the apparatus shown in Fig. 2. In bulb K hydrogen was added to the CO_2 sample and the mixture was converted into CO and H_2O by means of a hot platinum wire. The formed water was continuously condensed in the lower end of K which was cooled by Dry Ice. After the reaction was completed the CO together with the excess of H_2 was pumped off. The water was frozen into vessel E and electrolyzed. The obtained H_2/O_2 mixture could be pumped off through traps F_1 and F_2, cooled by liquid air and liquid hydrogen, respectively. Residual water vapor was frozen out in F_1 while the desired oxygen was condensed in F_2. The oxygen was filled into a pipet P from which it could be introduced into the mass spectrometer.

The results of all runs are given in Table II.[9] The reversing temperatures of the different combinations deduced from the readings in Table II are listed in Table III. Thus the unsymmetric molecule $O^{16}C^{12}O^{17}$ of mass 45 behaves exactly like the unsymmetric molecule $O^{16}C^{12}O^{18}$ of mass 46. Their common reversing temperature of 105° differs from that of the symmetric molecule $O^{16}C^{13}O^{16}$ of mass 45 by about 78°. The most satisfactory explanation of this behavior seems to be the above discussed influence of the symmetry number on the collision properties of the molecules.[10]

It appeared desirable to investigate the properties of the very rare CO_2 molecules 47 and 48 (see Table I). Of special interest was the behavior of the molecule $O^{18}C^{12}O^{18}$ which has the symmetry number 2: In contrast to $O^{16}C^{13}O^{16}$, having the heavy isotope in the center of gravity, $O^{18}C^{12}O^{18}$ has a moment of inertia different from that of the abundant $O^{16}C^{12}O^{16}$ with which all other molecules most probably collide. Results with $O^{18}C^{12}O^{18}$ would have answered the question whether a collision may be influenced essentially by a slight difference in the moments of inertia of the colliding particles. The *same* behavior of molecules $O^{16}C^{12}O^{17}$ and $O^{16}C^{12}O^{18}$ (see Table III), having *different* moments of inertia proves that such an influence, if it exists at all, must have a high peak if not be a discontinuous function of the difference in the moments of inertia. Such an effect, for example, may be due to a perturbation of rotational resonance.

In the attempt to increase the accuracy of measurement for the masses 47–48 by the use of C^{13} and O^{18} concentrates, it was found that in the metal tube[11] the oxygen atoms of CO_2 were exchanged in a few hours. This exchange took place although the CO_2 had been carefully dried by cooling it down to −80° before it was filled into the separator. Hence the concentrations of the rare molecules 47–48 followed almost completely the concentration shift of the abundant molecules 44–46. Therefore an investigation of the behavior of $O^{18}C^{12}O^{18}$ has not yet been possible. There is hope, that the problem can be tackled by use of a separating tube made of glass. At present the question must be left open, whether the different behavior of the symmetric and unsymmetric CO_2 molecules results essentially from the defect of rotational states or from the rotational resonance effect or some other effect of that kind.

We believe, however, to have shown that for quantum mechanical reasons the collision properties of a molecule can jump in an isotopic substitution, the change in the properties being nearly independent of the relative change in mass.

---

(6) W. W. Watson and D. Woernley, *Phys. Rev.*, **63**, 181 (1943).

(7) At a still higher mean temperature the thermal diffusion factor of 46/44 finally becomes greater than that of 45/44, which is to be expected because of the greater relative mass difference of the first pair (see run 8 of Table II).

(8) E. R. S. Winter. *Trans. Faraday Soc.*, **46**, 81 (1950).

(9) Most runs were done with technical CO_2, which in order to remove organic impurities had been glowed out with oxygen by means of a hot platinum wire. After this treatment it was fractionized with liquid air and Dry Ice. In order to make absolutely sure that the observed effects did not result from impurities, some typical runs were repeated with CO_2 prepared synthetically from NaCN (preparation method see E. W. Becker and W. Vogell, *Z. Physik*, **130**, 129 (1951)). They yielded the same values for the enrichment factors.

(10) A confirmation of this explanation is the fact that the mass combinations 45/44 and 46/44 of the principally unsymmetric molecule NNO show, according to our investigation, the *same* reversing temperature within the experimental error (115 ± 10°).

(11) The inner tube of the separator consisted of copper, the outer one of steel.

TABLE II

COMBINATION OF ALL EXPERIMENTS. $\overline{T}$ = ARITHMETIC MEAN TEMPERATURE OF THE HOT AND COLD WALL

Run No.	Pressure (atm.)	$\overline{T}$ (°C.)	ΔT (°C.)	Time (hr.)	A^{45}_{44}	$A^{16,13,16}_{44}$	$A^{16,12,17}_{44}$	$A^{16,12,18}_{44}$
1	4.5	41°	58°	482	1.040 ±0.005	...	...	0.77 ±0.01
2	5.0	68°	38°	565	1.072 ±0.004	1.081 ±0.004	0.960 ±0.005	0.929 ±0.004
3	4.5	82°	135°	247	1.166 ±0.007	...	...	0.94 ±0.01
4	5.5	91°	52°	532	1.099 ±0.005	...	...	0.965 ±0.006
5	5.5	93°	54°	480	1.108 ±0.004	1.108 ±0.004	0.999 ±0.006	0.983 ±0.005
6	5.5	139°	82°	485	1.258 ±0.005	...	...	1.146 ±0.007
7	5.5	140°	84°	473	1.277 ±0.006	1.298 ±0.006	1.04 ±0.01	1.14 ±0.01
8	5.5	214°	120°	812	1.54 ±0.01	...	...	1.63 ±0.01

TABLE III

REVERSING TEMPERATURES OF THE DIFFERENT MOLECULAR SPECIES OF CO_2

Molecule	$O^{16}C^{13}O^{16}$	$O^{16}C^{12}O^{17}$	$O^{16}C^{12}O^{18}$
Mass	45	45	46
Symmetry number	2	1	1
Reversing temp., °C.	27 ± 10°	105 ± 10°	105 ± 10°

The Behavior of Nuclear Isomers.—The described experiments suggest an investigation, which although not being in direct connection with the original problem, will be of a more general theoretical interest. It concerns the question, whether nuclear isomers are or are not "identical" particles in the quantum mechanical sense. The question might be answered *spectroscopically* by investigating whether the defect of rotational levels occurring in a symmetric molecule remains, if one of the identical nuclei is substituted by an isomer. For reasons of intensity, however, it would be necessary to introduce the isomer with a concentration comparable to that of the stable nucleus, which, up to date, has not yet been possible.

With the described thermal diffusion method that restriction does not exist. For such an investigation the concentration of the isomer must only be high enough, so that the isomer can be detected quantitatively by its radioactivity. The separator would have to be filled with a gas consisting of molecules with a certain symmetry. To a low extent molecules should be present, identical with the others except for the substitution of one of the identical nuclei by an isomer. Hereby the symmetry of the substituted molecules is lowered. If nuclear isomers are "not identical" in the quantum mechanical sense the defect of rotational levels will not occur with the substituted molecules. The consequence would be a difference in the specific radioactivity at the ends of the separator. If, on the other hand, the isomers are "identical" such a difference should not occur.

We are indebted to Professor W. Walcher for his interest in the work.

PROTON AND DEUTERON TRANSFER OVER HYDROGEN BRIDGES AS CAUSE OF CONDUCTIVITY EFFECTS

BY A. GIERER AND K. WIRTZ

Max Planck Institute for Physics, Göttingen, Germany

Received March 6, 1952

Previous data on the anomalous mobility of H^+ and OH^- in water and our own experiments on D^+ and OD^- in D_2O are analyzed. The hypothesis that a transfer of protons over hydrogen bridges between associated molecules in liquid water is the cause for the large mobilities is formulated quantitatively with the help of Eucken's data on the number of polymers in water. A complete description of the dependence on temperature between 0 and 300° is attained. The energies of activations for the transfer over the bridges are $q_{H^+} = q_{D^+} = 2440$ cal. mole^{-1}; $q_{OH^-} = 3020$ cal. mole^{-1}; $q_{OD^-} = 3130$ cal. mole^{-1}. The deviations from the linear interpolation of the mobilities in H_2O and D_2O are explained according to Baker and La Mer and calculated with the help of independent data of Schwarzenbach. The results favor Eucken's new parameters for the structure of water. We have expressed these parameters in numbers of hydrogen bridges in three different types of structures that are in close analogy to the three well known forms of coördination in water of Bernal and Fowler.

(1) **The Problem.**—Our work started from certain problems of hydrogen bonds. One question was as to whether physicochemical effects can be observed which are connected with the shift of protons (or deuterons) over H-bridges. This question was related to a hypothesis of the role of so called "systems" of H-bridges in proteins[1] as well as with some considerations concerning processes of the exchange of places in liquids.[2] It will be seen that both aspects are connected with the following work.

It has long been supposed that the abnormally large mobilities of OH_3^+ and OH^- ions in water are connected with a special mechanism of proton conductivity, the so called Grotthus mechanism, which involves transfer of protons over H-bridges between two associated molecules or molecular complexes, in the form

$$—H_2OH^+ + OH_2 \longrightarrow H_2O + HOH_2^+$$

$$\begin{matrix}H\diagdown & & & \diagup H & & H\diagdown & & & \diagup H\\ & O—H^+\cdots O & & & \longrightarrow & & O\cdots H^+—O & & \\ H\diagup & & & \diagdown H & & H\diagup & & & \diagdown H\end{matrix} \qquad (1)$$

This idea has been tried several times[3-6] without quantitative success, mainly because of the impossibility of calculating the probability for transfer over a H-bridge, especially as a function of temperature. The difficulties were such that attempts were even made to deal with the problem without the help of a proton transfer mechanism.[7]

(2) **Conditions for a Real Conductivity by Proton Transfer.**—We consider that hydrogen ions in water may have the form OH_3^+ and that hydroxyl ions OH^- may be associated similarly. The following considerations are valid for both ions so that we may restrict ourselves to hydrogen ions. In an electric field the OH_3^+ ion has a normal Stokes mobility corresponding to his hydration. Knowledge about motion processes in liquids favors the opinion that this mobility is of the same order as that of other ions of comparable dimensions such as the Na^+ ion. A mechanism of extra mobility of the supposed type requires that this slowly moving OH_3^+ ion is occasionally associated through a H-bridge, or more exactly uses one of its three equivalent protons as "donator" in linking with a neighboring H_2O molecule. The proton may jump over the bridge in the sense of (1), moving a distance corresponding to the distance between the two O-atoms. These jumps will occur preferably in the direction of an applied electric field, thus giving an extra mobility *u*. This extra mobility is (for ions of both signs)

$$u^{\pm} = u^{\pm}_{\text{obsd}} - u^{\pm}_{\text{Stokes}} \approx u^{\pm}_{\text{obsd}} - u_{\text{Na}^+(\text{or Cl}^-)} \qquad (2)$$

This idea is not new but is found partly in the work of Bernal and Fowler.[3] We now wish to formulate special conditions with which we can calculate quantitatively that part of the conductivity which depends on proton transfer: (a) What is the frequency of the formation of a hydrogen bond between OH_3^+ and a neighboring H_2O? (b) What is the frequency of "jumps" of a proton over this bridge and how does this frequency depend on the electric field? (c) After a jump in the direction of the field a molecular configuration remains that is not favorable for another jump in the same direction, either with respect to the bridge itself or, after their dissociation, with respect to the remaining H_2O (*cf.* (1)). For another favorable jump there must be some kind of "reorientation." What is the mechanism of "reorientation" in the case of real stationary conductivity over H-bridges? (d) Which of these steps is rate-controlling? Another question, *viz.*, are there conductivity effects, which yield no real conductivity because of an absence of reorientation may also be raised.[1]

(3) **The Probability for the Formation of Linear H-Bridges.**—We make the hypothesis that the probability for formation of linear H-bridges $H_2OH^+ \ldots OH_2$ is proportional to the stationary number of bridges in "linear" associated molecules. Eucken[8] has analyzed the structure of water from the following points of view: (a) Anomalies in the density of liquid water are produced by the fact that there is *one* form of association which is ice-like and has a volume 10% per molecule greater than other molecules in the liquid. The greater volume of the ice-like form comes from the fact that several molecules are connected by hydrogen

---

[1] K. Wirtz, *Z. Naturforsch.*, **2b**, 94 (1947); **2a**, 264 (1947); *Z Elektrochem.*, **54**, 47 (1950).

[2] K. Wirtz, *Z. Naturforsch.*, **3a**, 672 (1948).

[3] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[4] E. Hückel, *Z. Elektrochem.*, **34**, 546 (1928).

[5] G. Wannier, *Ann. Physik*, [5] **24**, 545 (1938).

[6] M. L. Huggins, THIS JOURNAL, **40**, 723 (1936).

[7] J. J. Hermans, *Rec. trav. chim.*, **58**, 917 (1939).

[8] A. Eucken, *Nachr. Ges. Wiss. Göttingen, math.-phys., Kl* (1946). S.38 u. (1949.) S.1 P; *Z. Elektrochem. angew. phys. Chem.*, **52**, 255 (1948).

bonds in a closed cyclic structure. (b) In order to explain anomalies in the heat capacity of water one has to introduce linear forms in addition to cyclic ones. These contribute little to anomalies of the volume, but by their heat of association contribute to anomalies in heat quantities in a similar way as the cyclic forms. (c) A certain fraction of molecules is not associated or in other words, a certain fraction of possible bridges is broken.

One more statement can be derived from ultrasonic absorption of water[9]: (d) The mean lifetime of a H-bridge is very short ($\sim 10^{-11}$ sec.). Every molecule is continuously changing its state of association.

These three types of "polymers" are in close analogy to those of Bernal and Fowler as is demonstrated by the following table:

Structures of Eucken	Structures of Bernal–Fowler	Number of bridges per molecule
Cyclic systems (ice-like)	Tridymite-like	γ'
Linear systems	Quartz-like	γ
Broken bridges	Close packing	$2-\gamma'-\gamma$

Eucken has analyzed the thermal and volume data of water in the sense of points (a) to (c). His results for the number γ' of H-bridges per molecule in the cyclic and γ in the linear form are given in Table I for H_2O and D_2O.[10] It is remarkable that the number of broken bridges $2\text{-}\gamma\text{-}\gamma'$ is relatively large at all temperatures; 2 is the highest possible number of bridges per molecule.

TABLE I

NUMBER OF H-BRIDGES PER MOLECULE IN LIGHT AND HEAVY WATER[a]

γ' in cyclic polymers; γ in linear polymers

	γ'		γ	
T, °C.	H_2O	D_2O	H_2O	D_2O
0	0.360	0.416	0.390	0.366
20	.218	.250	.443	.435
40	.121	.140	.465	.450
60	.062	.066	.463	.468
80	.035	.030	.442	.451
100	.016	.014	.418	.420
120	.006		.375	
160	.001		.314	
200	...		.275	
374	...		.112	

[a] The absolute values may have been an error of 10 to 20%. For calculations it is often convenient to know the precise relative values.

(4) **Mechanism of Extra Mobility.**—A jump of a proton over a H-bridge is assumed to be "normal," *i.e.*, the dependence on temperature is of the type

$$j = j_0 \times \exp(-q/RT) \qquad (3)$$

j being the number of jumps per sec. per proton and q the energy of activation. An electric field F modifies the energy of activation

$$q - (eFd \cos \vartheta)/2 \text{ in the direction } \vartheta \text{ with the field} \qquad (4)$$
$$q + (eFd \cos \vartheta)/2 \text{ in the direction } \vartheta \text{ opposite to the field}$$

e = charge, d = distance of the jump, ϑ = angle between field and bridge. The corresponding part of the conductivity is the excess Δj of jumps in the direction of field times the mean distance of the jumps in the direction of the field and times the probability γ of finding a *linear* bridge. (Cyclic systems don't take part in the conductivity effects.) This yields, written for both signs[11]

$$\begin{aligned} u^{\pm} &= \overline{\Delta jl \cos \vartheta \ \gamma} = u_0^{\pm} \ \gamma \times \exp(-q^{\pm}/RT) \\ u_0^{\pm} &= (j_0^{\pm} l^2)/(6kT); \ l \sim 2.8 \text{ Å}. \end{aligned} \qquad (5)$$

q and j_0 are not known; usually j_0 is considered to be connected with the frequency of oscillation of the proton. (5) is not quite exact but is sufficient for our purposes.

If (5) is correct, the extra mobility $u^{\pm}$ depends in a complex manner on outer parameters, especially on the temperature, namely, through γ as well as through $\exp(-q/RT)$. γ decreases with T, the exponential is increasing. But according to (5) the expression

$$\ln(u^{\pm}/\gamma) - \ln T \equiv \varphi^{\pm}(T) \qquad (6)$$

should depend linearly on $1/T$. The experimental data (Table II) behave exactly in this manner as is shown in Fig. 1. One obtains moreover from the experiments the results given in Table II.

TABLE II

OBSERVED EXTRA MOBILITIES FOR H^+ AND OH^- IN CM.^{2} × OHM^{-1} × MOLE^{-1} [12]

T, °C.:	0	18	25	50	75	100	128	156	218	306
u^+ :	199	270.5	299	383	449	489	519	528	501	344
u^- :	64.9	106.5	111.5	168	200	231	261	274	295	...

$$\begin{gathered} u_0^+ = u_0^-; \ j_0^+ = j_0^- = 2700 \text{ cm.}^{-1}; \\ q^+ = 2440 \text{ cal. mole}^{-1}; \ q^- = 3020 \text{ cal. mole}^{-1} \end{gathered} \qquad (7)$$

It is remarkable that the same factor γ holds for both ions. This means that even if the concentrations γ are modified by the ions they remain equal and proportional to the γ of neutral water. In Fig. 2 a comparison is made between the observed and the calculated extra mobilities.

The reorientation of the H_2O molecules is caused by temperature. For 0.1 N HCl there are 500 H_2O for every H^+, so that every H_2O has on the average $500/j \approx 10^{-9}$ sec. for the reorientation until the next jump. The actual time for reorientation to a statistical position is much shorter as is known from dielectric measurements. Finally question (c) can be answered: The rate is controlled by the process with the activation energy q.[13]

We may add that also the anomalous dependence on pressure of the extra mobility (increase with increasing p) can be explained by the increase of γ with p: voluminous ice-like structures are changed to linear ones.

(5) **Isotope Effects.** (a) **D^+-Ion.**—We have measured the conductivities of D^+ and OD^- in D_2O as a function of temperature[14] and analyzed the data

---

(9) L. Hall, *Phys. Rev.*, **73**, 775 (1948).

(10) A. Gierer and K. Wirtz, *Z. Naturforsch.*, **5a**, 577 (1950).

(11) A. Gierer and K. Wirtz, *Ann. phys.*, [6] **6**, 257 (1949).

(12) Johnston, *J. Am. Chem. Soc.*, **31**, 1025 (1909); A. A. Noyes, *Z. physik. Chem.*, **70**, 356 (1910).

(13) It may be stated that it is not certain whether the rate-controlling step connected with q is not the dissociation of the bridge, and the value $(eFd \cos \vartheta)/2$ is not simply the probability of the proton to be on one side of the bridge or the other, the barrier within the bridge being small. None of our formal conclusions would be changed by this interpretation. q would be the energy of activation for the dissociation of the bridge in this case.

(14) A. Gierer, *Z. Naturforsch.*, **5a**, 581 (1950).

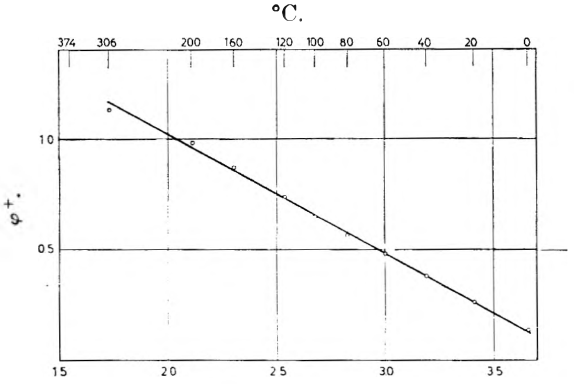


Fig. 1.— $\varphi^+ \equiv u^+/\gamma - \ln T$ *versus* $1/T$.

in a similar manner. Equation (5) should describe the effect, but the parameters should be modified. If j_0 is connected with the oscillations of the proton, then

$$(j_0)_{H_2O}/(j_0)_{D_2O} = (u_0)_{H_2O}/(u_0)_{D_2O} = \sqrt{2} \qquad (8)$$

From Table I one gets $V = (\gamma_{H_2O})/(\gamma_{D_2O})$ as given in Table III. At low temperatures V shows a few per cent. difference from 1 corresponding to the fact that D_2O contains more ice-like structure. Therefore one expects the relation

$$\overset{+}{u}_{H_2O}/\overset{+}{u}_{D_2O} = \sqrt{2}V \times \exp(-(\overset{+}{q}_{H_2O} - \overset{+}{q}_{D_2O})/RT) \qquad (9)$$

The observed results (Table III) show that the exponential expression is exactly unity, and therefore

$$\overset{+}{q}_{H_2O} = \overset{+}{q}_{D_2O} \qquad (10)$$

From the above discussion it follows that (5) also holds for D^+ in D_2O.

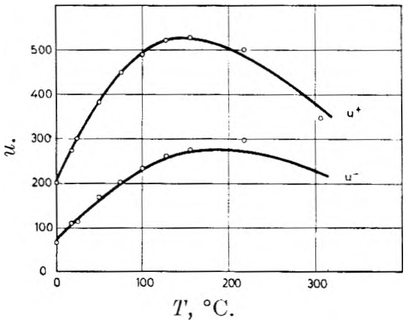


Fig. 2.—Points, observed extra mobilities; curve, calculated according to (5).

(b) **OD^- Ion.**—In the comparison of the observed conductivities of the OD^- ion with theory, the difficulty arises that the extra mobility is about equal to the normal one, and that the result depends sensibly on the amount of Stokes-mobility subtracted from γ_{OD^-} to get u^-. If one writes

$$\log(u^+/u^-) = \log(u_0^+/u_0^-) - 0.434(q^+ - q^-)/RT \qquad (11)$$

and requires as in the case of H_2O that $u_0^+ = u_0^-$, then one gets from the analysis of the experiments

$$u^- = \lambda_{NaOD} - 0.9\lambda_{NaCl} \qquad (12)$$

These values are given in Table III, and they give with (11)

$$q^+ - q^- = 690 \text{ cal. mole}^{-1} \qquad (13)$$

a result differing from that in H_2O only by ~100 cal. mole^{-1}.

TABLE III

EXTRA MOBILITIES IN D_2O IN CM.^{2} × OHM^{-1} × MOLE^{-1}

T, °C.	u^+	u^-	V	$\frac{\overset{+}{u}_{H_2O}}{u_{D_2O}} \times \frac{1}{\sqrt{2}}$
5	146.5	41.8	1.05	1.06
18	187.8	54.7	1.02	1.02
25	208.0	62.4	1.02	1.013
50	272.1	91.3	1.00	0.993
75	319.5	119.5	0.99	0.993
90	341.4	135.1	0.99	0.997
95	346.4	138.0	0.99	0.996

If the transfer of a proton or deuteron over a bridge is the rate-controlling step, the difference between the activations of H^+ and OH^- can be produced by the fact that in the case of OH^- the residual molecules between which the proton jumps are charged. That is not the case for the jumps of H^+. That $q_{D^+} = q_{H^+}$, but $q_{OD^-} > q_{OH^-}$, means therefore that only these additional effects are different in H_2O and D_2O, and only with the small amount of ~ 100 cal. mole^{-1}.

(6) **Isotope Effects in Mixtures of H_2O and D_2O.**—For normal ions such as Na^+ and Cl^-, the conductivity in H_2O and D_2O is within 1% proportional to the molar fraction of D_2O and H_2O. For ions with extra mobility there are considerable deviations from linearity, as has been found by Baker and La Mer.[15] Their explanation was that unsymmetrical transitions like

$$H_3O^+ + HDO \longrightarrow H_2O + H_2DO^+ \qquad (14)$$

are less frequent than symmetrical ones

$$H_3O^+ + H_2O \longrightarrow H_2O + H_3O^+ \qquad (15)$$

If this is correct, one can calculate the dependence of $\bar{u}/u$ ($\bar{u}$ = linear interpolation, u = observed value) on the temperature in the following manner. One can expect for the unsymmetrical transitions certain additional activation energies Δq_i: and perhaps heats of reaction ΔQ_i: which influence rates and concentrations. For a first approximation

$$\bar{u}/u = f(\Delta Q_i/RT; \Delta q_i/RT) = 1 + (G_i\Delta Q_i + g_i\Delta q_i)/RT = 1 + \Delta q/RT \qquad (14)$$

g_i and G_i being constants in the development. Therefore one expects a characteristic decrease of the deviation from 1 with increasing T. In Fig. 3 a comparison is made of the measured u/u for a 50% mixture and an interpolating straight line reaching $u/u = 1$ for $1/T = 0$, indicating that (14) is a good

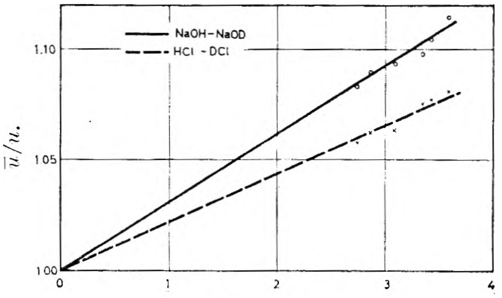


Fig. 3.—Deviation of the extra mobility u in mixtures of 50% H_2O and D_2O from the linear interpolated value $\bar{u}.u/u$ *versus* $1/T$ gives a straight line through zero.

---

[15] N. Baker and V. K. La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

approximation. The lines give $\Delta q^+ = 86$ cal. mole^{-1} and $\Delta q^- = 122$ cal. mole^{-1}.

The question remains whether one can calculate u/u from independent data. This was possible for the positive ion with the help of the work of Schwarzenbach[16] and Reitz.[17] From their researches on the acid and base constants of weak acids and bases in mixtures of H_2O and D_2O the equilibrium constants of reactions like (14) and (15) can be derived. It is concluded that the activation energies for the unsymmetrical transitions are nearly equal to the corresponding reaction heats, and that with respect to (9) all symmetrical transitions have the same energy of activation. By consideration of all possible transitions between all possible isotopic complexes and of their weights, the value of $(u/u)^+$ is calculated to be 1.055 at 25° where the experimental value is 1.072. This proves the idea of Baker and La Mer to be correct within the limits of the calculations.

Similar experiments are in progress on the extra mobility of H^+ and OH^- in other liquids containing hydrogen bridges.

[16] C. Schwarzenbach, *Z. Elektrochem. angew. phys. Chem.*, **44**, 46 (1938).

[17] O. Reitz, *Z. phys. Chem.*, **A176**, 363 (1936).

RELATIVE RATES OF HYDROLYSIS OF UREA CONTAINING C^{14}, C^{13} AND C^{12}

By JOHN A. SCHMITT, ALBERT L. MYERSON AND FARRINGTON DANIELS

University of Wisconsin, Department of Chemistry, Madison, Wisconsin

Received June 13, 1952

Urea containing C^{12}, C^{13} and C^{14} was hydrolyzed in the presence of urease. The relative rates of reaction were followed by the mass spectrometric analysis of the carbon dioxide which was evolved at successive time intervals. The heavier isotopes react more slowly, the C^{13} accumulating in the last fraction to decompose, and the C^{14} accumulating still more in accordance with the following ratios of the rate constants: $k_{C^{12}\text{-urea}}/k_{C^{13}\text{-urea}} = 1.010 \pm 0.001$ and $k_{C^{12}\text{-urea}}/k_{C^{14}\text{-urea}} = 1.032 \pm 0.002$.

Introduction

The hydrolysis of urea to give carbon dioxide and ammonia involves the breaking of bonds in which one would expect the reaction rates to follow the order $N\text{-}C^{12} > N\text{-}C^{13} > N\text{-}C^{14}$, in accordance with predictions based on the influence of isotopic mass differences on the zero point energy and the relative activation energies.[1] The hydrolysis of urea in the presence of urease is a complicated phenomenon, but the behavior of C^{12}, C^{13} and C^{14} should all be the same except for the isotopic effects. It was the object of this investigation to measure the change in isotopic ratios throughout the course of the reaction and thus determine the relative rates of reaction under identical conditions.

Experimental Procedure

The urea was dissolved in 15 ml. of a sodium acetate-acetic acid buffer with a *p*H of 5.0 and placed in a 1 × 8-inch test-tube immersed in a thermostat at 30.0°. In Expt. I with C^{13} and C^{12}, 0.1371 g. of Mallinckrodt analytical reagent was used; in Expt. II with C^{12}, C^{13} and C^{14}, 0.0537 g. of Mallinckrodt urea plus 0.0213 g. of C^{14}-urea as obtained from the U.S. Atomic Energy Commission at Oak Ridge was used. This urea containing radioactive carbon was equivalent to 1 millicurie and had about 5.5 atom % C^{14}.

A constant stream of CO_2-free nitrogen was bubbled through the solution of urea at a rate of 100–120 ml. per minute using finely fritted glass discs to give small dispersed bubbles. All the dissolved carbon dioxide was driven from the solution for about 20 minutes, and 50 mg. of jack bean urease in 5 ml. of buffer solution was then added, together with a few drops of capryl alcohol to minimize frothing. The stream of nitrogen was then passed through a three-way stopcock and into one of two standardized absorbing solutions containing sodium hydroxide and barium chloride where the carbon dioxide from the hydrolyzed urea was precipitated as barium carbonate.

The absorbing solutions were protected with ascarite from back diffusion of carbon dioxide in the air. When phenolphthalein in an absorption tube became nearly colorless the flow of exit gas was shifted to the other absorbing solution, and the barium carbonate was centrifuged and rinsed with cold water.

The barium carbonate precipitate from each successive fraction of the hydrolysis was treated with a supply of 60% perchloric acid using a rotating ground glass joint. The carbon dioxide liberated was collected with the help of a Toepler pump in gas sample tubes with stopcocks which had been thoroughly evacuated. These tubes with standard joints were then attached to the mass spectrometer. The $C^{13}O_2/C^{12}O_2$ and $C^{14}O_2/C^{12}O_2$ values were obtained by measuring both the 45/44 and the 46/(44 + 45) mass ratios for each sample, using a Consolidated-Nier isotope-ratio spectrometer. A large standard of barium carbonate was used as a reference against which to check the successive samples. The usual corrections for O^{17} and O^{18} were applied to the spectrometer readings.

In Expt. I (Table I) the total time taken for the first twelve samples, comprising about 93% of the total decomposition, was three hours. The thirteenth sample comprising the last 6.67% of the gases evolved in the reaction, $CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$ was collected after the reaction was permitted to proceed for 15 hours more.

Experiment II with radioactive urea from Oak Ridge was complicated by the fact that the rate of hydrolysis slowed down abnormally and it became necessary to add more urease four times during the course of the reaction. This inhibition of the hydrolysis may possibly have been due to a poisoning of the urease by unknown, heavy metal ions present in the C^{14}-urea.[2] When normal Mallinckrodt urea was used under the same conditions there was no inhibition of the urease. The introduction of additional urease during the course of the reaction resulted in inaccuracies and the loss of some of the fractions from dilution with carbon dioxide from the air.

Results

Preliminary experiments showed that the lighter isotope of carbon reacts faster and the heavier ones concentrate in the unreacted remainder of the urea. The results of more accurate measurements are shown, Expt. I with Mallinckrodt urea in Table I

---

[1] F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, pp. 248–250.

[2] J. B. Sumner and K. Myrbäck, "The Enzymes," Vol. I, Academic Press, Inc., New York, N. Y., 1951, p. 882.

and Fig. 1, and Expt. II with Oak Ridge urea in Table II and Fig. 2. In the figures, C^{13}/C^{12} and C^{14}/C^{12} ratios are plotted against the per cent. of the urea which has reacted. Since each sample represents an average ratio for all the carbon dioxide collected over the whole interval the point in the middle of the interval was used in plotting the per cent. of reaction completed.

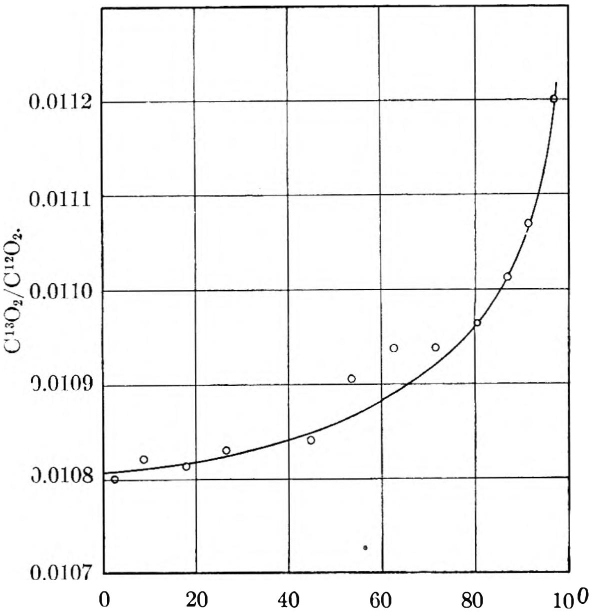


Fig. 1.—Relative amounts of $C^{13}O_2$ and $C^{12}O_2$ evolved during the hydrolysis of urea with urease.

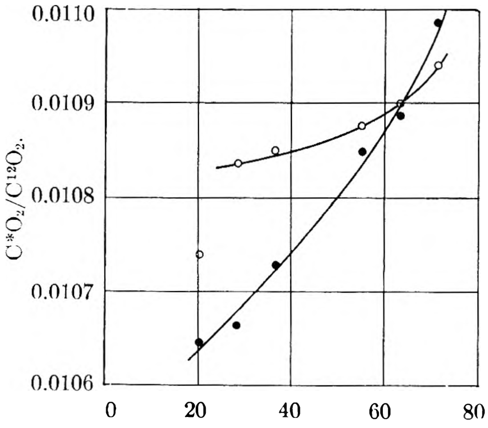


Fig. 2.—Relative amounts of $C^{13}O_2$ (or $C^{14}O_2$) and $C^{12}O_2$ evolved during the hydrolysis of urea with urease: ○, $C^{13}O_2/C^{12}O_2$; ●, $C^{14}O_2/C^{12}O_2$.

In Expt. II there were experimental difficulties which led to the loss of several readings, including that of the last fraction in which the reaction mixture frothed over.

Calculations

Equation (1)[3] may be used to calculate the relative rates of hydrolysis of C^{12}- and C^{13}-urea.

TABLE I

HYDROLYSIS OF MALLINCKRODT UREA IN THE PRESENCE OF UREASE

Fraction	$C^{13}O_2/C^{12}O_2$	Atom % C^{13}
0.000–0.044	0.01080	1.068
.044– .133	.01082	1.071
.133– .222	.01081	1.070
.222– .311	.01083	1.071
.311– .400	(.01084)[a]	(1.072)[a]
.400– .489	.01084	1.072
.489– .578	.01091	1.079
.578– .667	.01094	1.082
.667– .756	.01094	1.082
.756– .845	.01096	1.084
.845– .889	.01101	1.089
.889– .933	.01107	1.095
.933–1.000	.01120	1.108

[a] Developed an air leak in the gas sample tube. Values given in parentheses are taken from the curve of Fig. 1 for the purpose of summing.

TABLE II

HYDROLYSIS OF C^{14}-LABELED UREA IN THE PRESENCE OF UREASE

Fraction	$C^{13}O_2/C^{12}O_2$	$C^{14}O_2/C^{12}O_2$
0.163–0.245	0.01074	0.01065
.245– .327	.01084	.01066
.327– .408	.01085	.01073
.510– .592	.01088	.01085
.592– .674	.01090	.01089
.674– .755	.01094	.01098

$$\log \frac{N_0}{N} = \alpha \log \frac{V}{V_0} \qquad (1)$$

where

N_0 = amount of reactant (C^{13}) in the initial material
N = amount of reactant (C^{13}) in the final unreacted material
V_0 = original quantity of material
V = final quantity of unreacted material
α = $k/k^* - 1$ where k/k^* = the ratio of the reaction rate constant of the lighter isotope to that of the heavier isotope

Applying (1) to the data of Table I, using the atom % of the final sample for N (assuming complete reaction) and a sum obtained from all the individual readings for N_0. $\alpha = 0.0096$. Then the relative rate of hydrolysis of C^{12}- and C^{13}-urea is $k_{C^{12}\text{-urea}}/k_{C^{13}\text{-urea}} = 1 + \alpha = 1.010$.

The data of Table I can also be fitted into the equation of Bothner-By and Bigeleisen.[4]

$$\log \left[1 + \frac{N_{X^0} - N_X}{N_{X^0}} \times \frac{f}{(1-f)}\right] = \left(\frac{k_3}{k_1} - 1\right) \log (1 - f) \qquad (2)$$

where

f = the fraction of reaction of the initial material
N_X = $C^{13}O_2/C^{12}O_2$ of the cumulative CO_2 sample collected up to f
N_{X^0} = $C^{13}O_2/C^{12}O$ of the cumulative CO_2 sample at $f = 1$
$\frac{k_3}{k_1}$ = ratio of the rate of formation of $C^{13}O_2$ to that of $C^{12}O_2$

N_X values corresponding to f values are obtained by proper summing of the data in columns 1 and 2

---

(3) F. Daniels, ref. 2, p. 251.

(4) A. A. Bothner-By and J. Bigeleisen, *J. Chem. Phys.*, **19**, 755 (1951).

of Table I. A plot of log $[1 + N_X{}^0 - N_X/N_X{}^0 \times f/1 - f]$ *vs.* log $(1 - f)$ was constructed. A good straight line was obtained over the range $f = 0.00$ to 0.93. From the slope of this line $k_3/k_1 - 1 = -0.00986$ and $k_{C^{12}\text{-urea}}/k_{C^{13}\text{-urea}} = k_1/k_3 = 1.010$, the same value obtained above.

Using the definition of Bigeleisen[4] for N_X and f, and adding $W = C^{13}O_2/C^{12}O_2$ (or $C^{14}O_2/C^{12}O_2$) for the total CO_2 evolved during any fraction of the reaction between f_1 and f_2, it can be shown readily that for small changes in N_X

$$f_1 N_{X_1} + (f_2 - f_1)\, W = f_2 N_{X_2} \qquad (3)$$

where f_1 and f_2 represent the fractions of reaction before and after the evolution of a sample of CO_2 having an average $C^{13}O_2/C^{12}O_2$ value of W. From another form[4] of (2)

$$f_1 N_{X_1} = N_X{}^0\,[1 - (1 - f_1)^{k_3/k_1}] \qquad (4)$$

and

$$f_2 N_{X_2} = N_X{}^0\,[1 - (1 - f_2)^{k_3/k_1}] \qquad (5)$$

Substituting (4) and (5) in (3) and rearranging

$$(f_2 - f_1)\, W = N_X{}^0\,[(1 - f_1)^{k_3/k_1} - (1 - f_2)^{k_3/k_1}] \qquad (6)$$

For any two sets of points as obtained in this experiment where W_a is the $C^{13}O_2/C^{12}O_2$ (or $C^{14}O_2/C^{12}O_2$) value between f_1 and f_2 and W_b is the corresponding value between f_3 and f_4, (6) becomes

$$\frac{(f_4 - f_3)W_b}{(f_2 - f_1)W_a} = \frac{(1 - f_3)^{k_3/k_1} - (1 - f_4)^{k_3/k_1}}{(1 - f_1)^{k_3/k_1} - (1 - f_2)^{k_3/k_1}} \qquad (7)$$

This equation requires only the measurement of W values for known fractions of reaction. Neither $N_X{}^0$ nor the per cent. heavy isotope in the final residue need be known, so that (7) is suited to the calculation of relative reaction rates from the data in Table II.

Values of k_3/k_1 were calculated for each possible pair of points, first for $C^{13}O_2/C^{12}O_2$ and then for $C^{14}O_2/C^{12}O_2$.

The average value of $k_{C^{12}\text{-urea}}/k_{C^{13}\text{-urea}}$ for the ten possible solutions of (7) using all the points except the first is 1.010 ± 0.001. This value corresponds to that obtained from the data in Table I.

Similarly, the fifteen possible solutions of (7), using all the points in the table, result in an average value for $k_{C^{12}\text{-urea}}/k_{C^{14}\text{-urea}}$ of 1.032 ± 0.002.

Discussion

It has been clearly shown that the urea molecules containing C^{13} hydrolyze a little more slowly than those containing C^{12} and that those containing C^{14} hydrolyze still more slowly. The effect of C^{14} is greater than the effect of C^{13}. These findings are in agreement with theoretical predictions.[1]

The hydrolysis of urea was chosen to test these predictions because this reaction seemed to involve as a rate-determining step the breaking of the N–C bond, and because urea could be easily synthesized[5] on a microscale with ammonia and radioactive carbon dioxide from $BaC^{14}O_3$ available in 1947. In preliminary work, reported as an abstract from this Laboratory, the relative rates of hydrolysis appeared to be in the wrong direction.[6] The course of the isotopic reactions was followed by determining the radioactivity of the barium carbonate precipitated from the CO_2 evolved at intervals throughout the hydrolysis of the urea. We are at a loss to understand what experimental inadequacy could have caused the C^{14}/C^{12} ratio to appear lower in the last fractions of urea which hydrolyzed. The work described here was planned with larger quantities of C^{14} and with the use of a mass spectrometer for the simultaneous determination of all three isotopes of carbon under conditions which permit direct calculations.

The ratios of $k_{C^{12}\text{-urea}}/k_{C^{14}\text{-urea}} = 1.03$ and $k_{C^{12}\text{-urea}}/k_{C^{14}\text{-urea}} = 1.01$ are real and they are in the right direction, but the effects are smaller than predicted[1] on the basis of zero point energies: $k_{C^{12}\text{-urea}}/k_{C^{14}\text{-urea}} = 1.088$, and $k_{C^{14}\text{-urea}}/k_{C^{13}\text{-urea}} = 1.045$.[7] It is not surprising, however, that they are smaller because the calculated values were based on the assumption that the energy of the activated complex for C^{12}, C^{13} and C^{14} compounds are all the same and that the only difference in activation energies comes from the differences in zero point energies. This assumption may well be unwarranted. Moreover, the entropy of activation was assumed to be the same for all the isotopes, and this assumption also may well be unwarranted. Again, the presence of urease introduces a serious complication into the concept of the activated complex and the calculations of the activation energies. Bigeleisen[8] has considered much more thoroughly the effect of the C^{13}- and C^{14}-isotopes on the rate of chemical reactions but it seems difficult to apply his calculations to an enzymatic reaction such as the one studied in this investigation.

Efforts are now being made to study the isotope effect in the hydrolysis of urea carried out in the absence of urease.

Kinetic studies in this Laboratory on many other reactions check the findings of this investigation in showing that the C^{13} concentrates in the last portion of the material to react.

The authors are glad to acknowledge the support of the major part of this investigation through a grant from the Research Committee of the Gradu-

---

[5] A. L. Myerson, *J. Am. Chem. Soc.*, **74**, 2437 (1952).

[6] F. Daniels and A. L. Myerson, *Science*, **108**, 676 (1948).

[7] The fundamental frequency ν of the C^{12}–N bond is approximately 2.715×10^{13} sec.$^{-1}$. Assuming that the force constants are the same for C^{12}–N and C^{14}–N and that the only difference in frequency is due to the reduced mass

$$\frac{\nu_{C^{12}\text{-N}}}{\nu_{C^{14}\text{-N}}} = \left(\frac{14 \times 14}{14 + 14} \bigg/ \frac{12 \times 14}{12 + 14}\right)^{1/2} = 1.04.$$

Then

$$\nu_{C^{14}\text{-N}} = 2.608 \times 10^{13} \text{ sec.}^{-1}$$

The difference in zero point energy of the two bonds is

$$1/2\, h\,(\nu_{C^{13}\text{-N}} - \nu_{C^{14}\text{-N}}) = 50.6 \text{ cal. mole}^{-1}$$

Assuming that the entropies of activation and the frequency factors are the same for both bonds and that the only difference lies in the zero point energies, the ratio of the specific reaction rates of bond rupture at 30° is

$$\frac{k_{C^{12}-N}}{k_{C^{14}-N}} = e^{\frac{-50.6}{2 \times 303}} = 1.088$$

Using the same type of calculation for the C^{13}–N and the C^{12}–N bonds the difference in zero point energies is 26.5 cal. and

$$\frac{k_{C^{12}-N}}{k_{C^{13}-N}} = e^{\frac{-25.6}{2 \times 303}} = 1.045$$

[8] J. Bigeleisen, *J. Chem. Phys.*, **17**, 345, 675 (1949).

ate School with funds given by the Wisconsin Alumni Research Foundation. They are indebted to Professor Robert H. Burris and to the Thomas E. Brittingham Foundation for the use of the mass spectrometer. The work has been greatly facilitated through the purchase of C^{14}-labeled urea from the Isotopes Division of the Atomic Energy Commission.

DISTRIBUTION OF ALPHA RAY ENERGY IN RADIATION CHEMISTRY

By S. C. Lind

Carbide and Carbon Chemicals Company, Oak Ridge, Tennessee

Received July 23, 1952

Yield of acetylene polymerization in alpha particle bombardment of mixtures containing inert gases is proportional to the number of ions produced by the irradiation. Such excited atoms or molecules as are primarily produced by the bombardment apparently make no significant contribution to the yield.

It is well known that alpha particles expend only part of their energy in ionizing gases in which they are absorbed. Customarily it is assumed that the rest is spent in producing excitation. In radiation chemistry it has further been postulated that the excited states contribute to chemical action in addition to that brought about by ionization.

If in different gases the alpha ray energy divided itself in the same proportion between ionization and excitation it would be difficult to differentiate the two effects, especially since there is no direct method of measuring the number of excited states.

But fortunately for our purpose the distribution of energy is not always the same. In the rare gases the excess of energy beyond the ionization potential, which presumably would be available for chemical action caused by excitation, varies from 3.2 e.v. out of a total alpha ray energy of 27.8 e.v. in helium to 8.7 out of 20.8 e.v. for xenon; and in nitrogen 17 out of 35 e.v.

These differences of energy distribution (Table I) when linked with the discovery[1] that ions of any inert gas mixed with a chemically reactant gas (or gases) produce the same amount of chemical reaction as the ions of the reactant itself, furnish an answer to the question of the contribution made by the excess energy to the chemical yield. For example, if in pure acetylene 20 C_2H_2 molecules are polymerized per $C_2H_2^+$ ion produced by alpha rays, in a mixture of acetylene and argon the ion yield is again 20 C_2H_2 molecules but only if related to the total of $C_2H_2^+ + A^+$ ions. The same is true for a mixture of acetylene with any of the other inert gases and evidently means that the inert gas ions have the same ability to cause polymerization of acetylene as do the $C_2H_2^+$ ions. Here we are not concerned with the mechanism of the reaction but the existing experimental data (Table I) clearly show that correlation is satisfactory for the ion yield, and that there is no relation to the excess energy; where it is highest (N_2 and A) the ion yield is somewhat low, where excess energy is low (He and Ne) the ion yields are slightly higher.

Table I[2]

Alpha Ray Polymerization of Acetylene Mixed with Rare Gases

Gas[3]	Total energy per ion pair (1)	Ionization potential (2)	Excess energy (1) − (2)	Ratio (1):(2)	Energy yield predicted From mixture	Ion yield (M/N) found
He	27.8	24.58	3.2	1.13 × 19.8 =	22.4	19.7
Ne	27.4	21.56	5.9	1.27 × 19.8 =	25.2	19.2
N_2	35.0	15.58	18.0	2.24 × 19.8 =	44.3	18.5
A	25.4	15.76	10.1	1.6 × 19.8 =	31.8	18.2
Kr	22.8	14.00	9.8	1.63 × 19.8 =	32.3	19.6
Xe	20.8	12.13	8.7	1.72 × 19.8 =	34.0	18.0
				Av.	31.4	18.9
				Av. % dev.	16.6%	3.4%
				Yield for C_2H_2 alone		19.8

The sixth column of Table I (Energy yield predicted) assumes that the excess energy contributes to chemical action in the same proportion as does the energy of ionization. While this may not be a fair assumption, any other that would bring the predicted energy yields into satisfactory agreement would probably be an *ad hoc* distribution arbitrarily chosen to fit each inert gas separately and without any experimental or theoretical support.

Other gas reactions[1] also sensitized by the inert gases under alpha radiation give similar results. Polymerization of acetylene was chosen for the present discussion on account of the wealth of experimental evidence and the perfection of the reaction kinetics. A solid product without vapor pressure leaves the acetylene gas without interfering by-products.[4] Excellent kinetics are easily attained, but only by taking into quantitative account the changing conditions for ionization in the gas mixtures in which the inert gas remains unchanged and consequently becomes relatively enriched as the reaction proceeds.

---

(1) S. C. Lind and D. C. Bardwell, *Science*, **62**, 422, 593 (1925); **63**, 310 (1926); *J. Am. Chem. Soc.*, **48**, 1575 (1926); S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," 1928, p. 189.

(2) Table I was included in an unpublished review of theories of radiation chemistry given at the International Congress of Pure and Applied Chemistry, New York, September, 1951.

(3) Rutherford, Chadwick and Ellis, "Radiations from Radioactive Substances," Cambridge University Press, New York, N. Y., 1930, p. 81.

(4) Mund and Rosenblum (*J. Phys. Chem.*, **41**, 469, 651 (1937), *Bull. Soc. Chim. Belg.*, **46**, 503 (1937)) have found benzene to be a product of the reaction when carried out in large volume of acetylene with low intensity of alpha radiation. Under quite different conditions Lind and Bardwell observed no volatile products and obtained good kinetics from atmospheric pressure to practical exhaustion of C_2H_2 (a few mm.). If benzene is formed under these conditions (small volume and high intensity of radiation) it must quickly be polymerized without disturbing the kinetics.

CALORIMETRIC EVIDENCE FOR THE CAPILLARY CONDENSATION THEORY

By Izumi Higuti and Yoshitomo Iwagami

Chemical Institute, Faculty of Science, Tohoku University, Sendai, Japan

Received September 21, 1951

(1) Heat capacities of benzene sorbed in varying amount on SiO_2 gel or active charcoal, and of carbon tetrachloride on SiO_2 gel have been measured over a wide range of low temperatures. (2) Anomalously large heat capacities, which have been found in the case of silica gel, and due to the sorbate in a large amount have been attributed to melting of the sorbate. (3) Based on the difference in pore structures between silica gel and active charcoal, obtained by applying the Thomson equation to benzene isotherms on each of them at 0°, the inception of the freezing point depression of the sorbate in the case of silica gel and none in another has been explained reasonably. The radius (r) of pores in which the utmost amount of sorbate would melt with a definite increase of temperature has been determined in every experiment varying the amount sorbed. (4) Using the experimental value of r thus obtained and values of ρ, γ and ΔH in the literature, ΔT has been calculated by the theoretical formula $\Delta T/T_0 = 2\gamma M/\rho r\Delta H$, giving essentially a good agreement with ΔT, corresponding to the temperature where experiment shows melting of the maximum amount of the sorbate. (5) In view of the results obtained in this paper, together with those in the previous papers, it has been stressed that the sorption phenomena by porous solid should be divided into two processes; one, the so-called adsorption, concerning the interaction between the sorbate molecules and the surface of solid; the other, the capillary condensation, concerning the pore size distribution of porous solid, by which the shape of isotherms is determined essentially.

1. Introduction

In the previous paper,[1] dealing with the dielectric polarization of *n*-propyl alcohol and *i*-amyl alcohol sorbed on the porous titania gel, it was shown that the dielectric constant of the sorbate and its temperature coefficient exhibited a remarkable difference according to its equilibrium relative pressure. Also in the relative pressures above a critical value, the sorbate appeared as a liquid condensing in capillary pores because its dielectric polarization increased with descending temperature and exhibited an anomalous dispersion at still lower temperatures, such behaviors being similar to the property of the bulk liquid. In the succeeding papers,[2,3] dealing with the freezing phenomena of nitrobenzene[2] and *o*-nitrophenol[3] sorbed on silica gel by the same method, the freezing point depression of the sorbate in the high relative pressure range and its dependency on the radius of pores in which the sorbate condensed, were clearly ascertained. In addition, capillary radii of pores in which the sorbate would freeze at the chosen temperatures were obtained on the basis of the amount sorbed and the pore structure of the sorbent involved. The observed freezing point depression ΔT of the sorbate condensing in pores greater than a certain value (r) of radius was shown to give a good fit to the theoretical values calculated by the expression $\Delta T/T_0 = 2\gamma M/\rho r\Delta H$, which was derived[4] by thermodynamic consideration. All these findings give the most confirmative evidence for the capillary condensation theory for the sorption process. In this paper we shall present additional evidence from calorimetric measurements, *i.e.*, measurements of the freezing point depression of the sorbate (condensate) and its dependency on the radius of capillary pores. The satisfactory results thus obtained will place the theory on a firmer basis.

Culbertson and Winter[5] have already made calorimetric measurements of the sorption system and Patrick and Kemper[6] further found the freezing point depression for a number of sorbates on silica gel. However, without recognizing the radius of capillary pores as the most important parameter in the phenomenon, they failed to correctly interpret their experimental results. The present authors proceeded with their researches on sorbents for which the capillary pore size distributions were determined previously.

2. Experimental

(A) **Materials.**—Active charcoal and silica gel of commercial source and of 200 mesh size were used always after evacuating them at 250°, because with these sorbents isotherms of benzene at 0°, expectedly revealed suitable pore size distributions. Benzene was purified with concentrated sulfuric acid, then by distillation and crystallization several times. Carbon tetrachloride was treated with potassium hydroxide and alcohol. The purified substances were distilled three times in vacuum before sorption experiments were made.

(B) **Apparatus and Measuring Procedures.**—Isotherms of benzene were obtained, in a closed system with mercury cut, by means of a McBain and Bakr quartz balance and mercury manometer, as is usually done in this Laboratory in studying sorption isotherms of organic vapors. A conduction calorimeter was devised after referring to those constructed by Ziegler[7] and Patrick and Kemper[6] as schematically shown in Fig. 1. In the figure, A is a copper chamber containing a definite quantity of the sorbent, and B is a glass capillary tube which is connected to the vacuum pump system through a constricted part K, and to the sorbate reservoir through breakable joints, for supplying the sorbate vapor to the sorbent in succession. C is a tube to introduce the dry air into the main part of the apparatus during the measurements, in order to prevent the intrusion of moisture into the apparatus. E and F are the copper-constantan thermocouples, the former serves for measuring the temperature of the container of the sorbent, and the latter for keeping the constant temperature difference between A and G which is a copper cylinder, wound outside with heating nichrome wire. Glass tube B is likely to reduce the experimental accuracy. Notwithstanding this defect, with this apparatus we may have an advantage of determining directly the heat capacity contribution due to the varying amount of the sorbate successively. First, an

---

[1] I. Higuti, *Sci. Rep. Tohoku Univ. I*, Series **33**, 99 (1949); *Bull. Inst. Phys. Chem. Research*, **20**, 489 (1941); **21**, 1138 (1942).

[2] I. Higuti, *Sci. Rep. Tohoku Univ. I*, Series **33**, 174 (1949); *Bull. Inst. Phys. Chem. Research*, **23**, 565 (1944).

[3] I. Higuti and M. Shimizu, This Journal, **56**, 198 (1952).

[4] I. Higuti, *Sci. Rep. Tohoku Univ.*, I, Series **33**, 231 (1949); *Bull. Inst. Phys. Chem. Research*, **23**, 598 (1944).

[5] G. L. Culbertson and L. L. Winter, *J. Am. Chem. Soc.*, **63**, 95 (1941).

[6] W. T. Patrick and W. A. Kemper, This Journal, **42**, 369, 381 (1938).

[7] W. T. Ziegler and C. E. Messer, *J. Am. Chem. Soc.*, **63**, 2694 (1941).

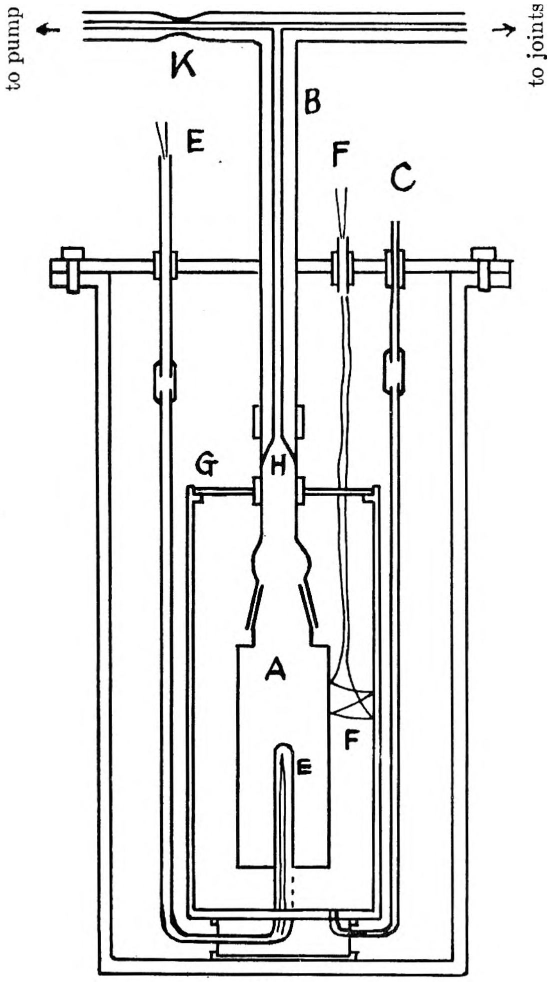


Fig. 1.

aliquot amount of the sorbent previously evacuated at 250° was placed in A. After connecting glass tube B, as shown in Fig. 1, and evacuating the whole system *in situ* for many hours, constricted part K was sealed off. After the whole calorimeter which was set in dewar flask was cooled down by liquid nitrogen, the temperature of A was slowly elevated by heating the outer cylinder G, keeping the temperature difference between A and G constant. If we plot the temperature enhancement of A during a definite time, say five minutes $(\Delta T/\Delta t)$, against the temperature of A, (T), it is easily understood that $(\Delta T/\Delta t)$ is inversely proportional to the relative heat capacity of the calorimeter with the sorbent. Following this experiment which is denoted as No. 1, an aliquot amount of the sorbate was introduced at room temperature through the breakable joint into the measuring system. After standing for some time to allow the sorption equilibrium, a similar measurement was carried out. A series of similar experiments was performed by successive addition of the sorbate and they are denoted by successive experimental numbers.

3. Results

(A) Isotherms of Benzene.—Isotherms of benzene at 0° on the active charcoal and the silica gel are represented in Fig. 2. The curve for active charcoal reaches its saturation value in the low pressure region, whereas in case of silica gel the main portion of the sorption process takes place in the relative pressure range from 0.4 to 0.8. On the basis of the Thomson equation and the experimental data obtained above, the capillary volume φ of pores whose radius is between r and $r + dr$ can be computed as a function of r. These pore structure curves or pore size distribution curves are shown in Fig. 3. A is for the silica gel and B for the active charcoal. According to a recently proposed theory,[8] the Thomson equation is inapplicable in the range of relative pressures lower than a certain value. Therefore the left-hand portions of A and B curves less than 10 Å. or so are exhibited merely for reference. From these figures, however, it is clear that the active charcoal used here has generally narrower pores in its structure, whereas in the silica gel capillary pores of radii from 25 to 80 Å. predominate. In the capillary condensation theory, the pore structure, characteristic for the nature of a porous solid, is of the utmost importance and its significance may be described in the next section.

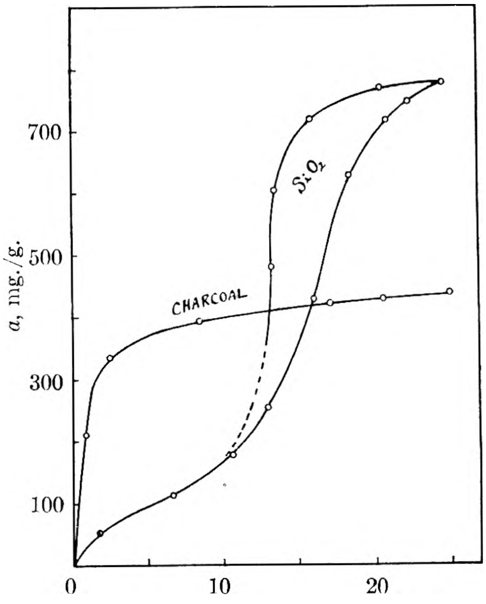


Fig. 2.—Isotherms of benzene.

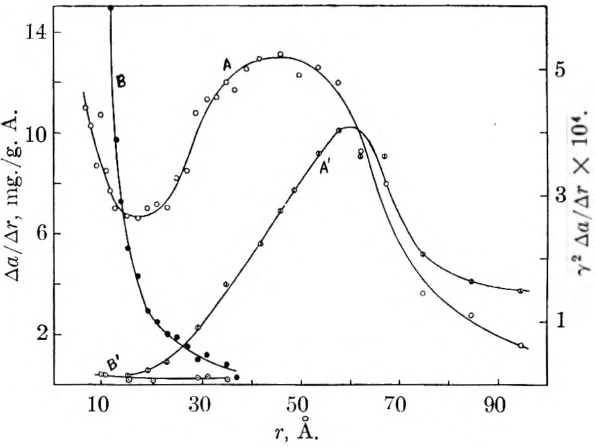


Fig. 3.

(B) Calorimetric Measurements.—In Figs. 4, 5, and 6 are represented the experimental results on heat capacities obtained with the various amounts of sorbate in sorption systems of $C-C_6H_6$, $SiO_2-C_6H_6$ and SiO_2-CCl_4. Experiment No. 0 corresponds to the system without either the sorbent or the sorbate. The obvious minimum at *ca.* 5.5° in curves No. 4 in Fig. 4 and No. 6 in Fig. 5 may certainly be attributed to the melting of free benzene, as there the presence of benzene is above the saturation value of sorption. However, there appears anomalous heat capacity in experiments No. 3 to 6 in Fig. 5 and No. 3 to 5 in Fig. 6 at temperatures lower than the normal melting point. These anomalous heat capacities, due to the increased sorbate, give the confirmative evidence, as Patrick and Kemper[6] once concluded, that the sorbate in frozen state melts at the respective temperature, because there is no transition in solid phase at least in the temperature range concerned. A slight kink at about −130° in curve of No. 2 in Fig. 6 may be attributed to the same phenomenon. Accordingly, the experiments may be considered to show the important fact that sub-

---

[8] I. Higuti, *Bull. Inst. Phys. Chem. Research*, **20**, 130 (1941).

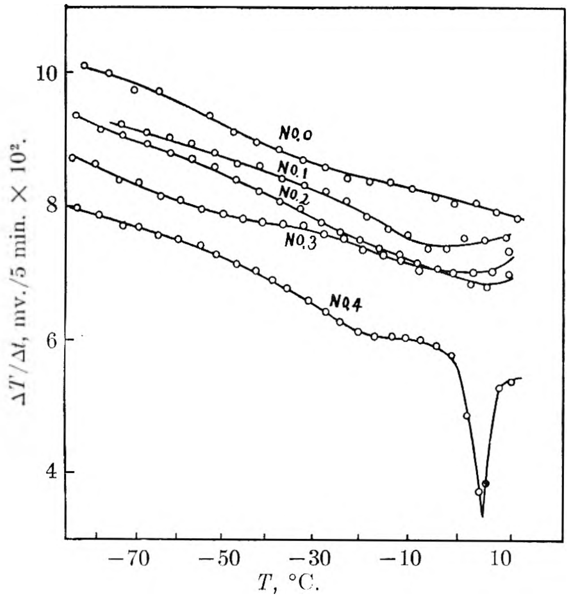


Fig. 4.—The relative heat capacity change due to the amount of benzene sorbed on active charcoal: No. 0, calorimeter alone; No. 1, with the sorbent alone; No. 2, 207 mg./g.; No. 3, 422 mg./g.; No. 4, 846 mg./g. of benzene.

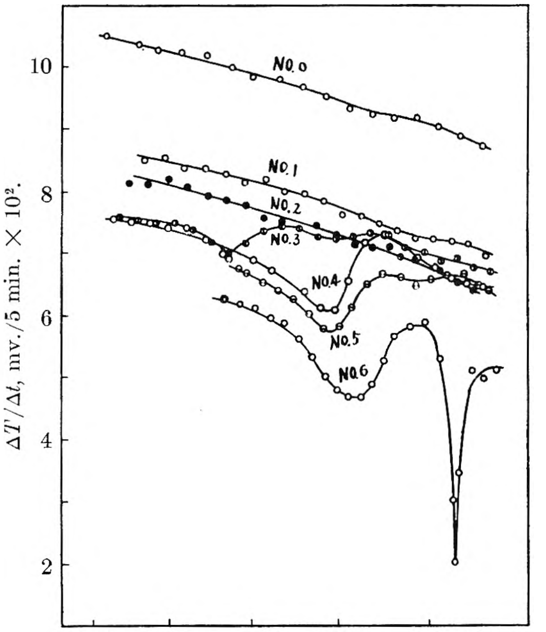


Fig. 5.—The relative heat capacity change due to the amount of benzene sorbed on silica gel: No. 0, calorimeter alone; No. 1, with the sorbent alone; No. 2, 189 mg./g.; No. 3, 387 mg./g.; No. 4, 568 mg./g.; No. 5, 740 mg./g.; No. 6, 1404 mg./g. of benzene.

stances in the sorbed state reveal the freezing point depression ΔT, and ΔT decreases as the amount sorbed increases, down to a certain value. The further shift observed in experiment No. 6 in Fig. 5 may probably have connection with a large excess of free benzene. In cases of experiment No. 2 in Fig. 5 and of all experiments in Fig. 4, though the experimental error seems considerable, we cannot recognize melting of the sorbate at least in the temperature range down to −70°. These various features of experimental results for melting of the sorbate, depending both on the amount sorbed and the sorbent, may be considered in detail in the later sections. The amount sorbed and the temperature (T_m) corresponding to the minimum in the respective curve are presented in Table I.

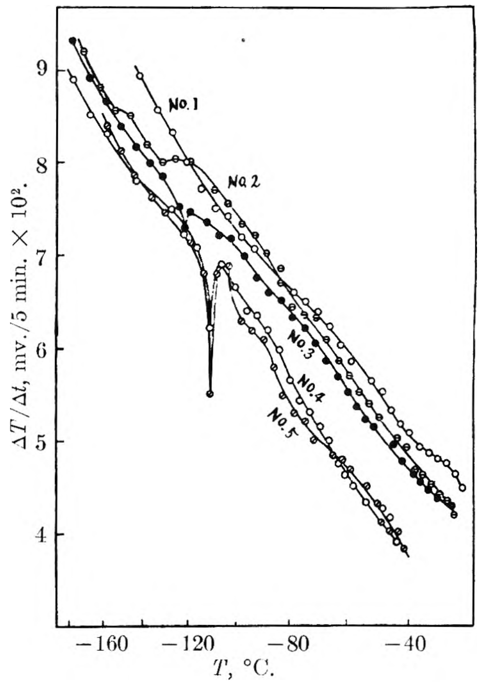


Fig. 6.—The relative heat capacity change due to the amount of carbon tetrachloride sorbed on silica gel: No. 1, with the sorbent alone; No. 2, 682 mg./g.; No. 3, 1024 mg./g.; No. 4, 1416 mg./g.; No. 5, 1892 mg./g. of the sorbate.

TABLE I

System	Expt. no.	Amount sorbed, mg./g.	T_m, °K.	ΔT	r
SiO_2-C_6H_6	2	189	. . .	. . .	(28)
	3	378	223.7	50.6	43
	4	568	257.0	27.3	59
	5	740	257.7	26.6	60
	6	1404	263.2	21.1	60
SiO_2-CCl_4	2	682	141.6	107.7	39.5
	3	1024	151.9	97.4	52.7
	4	1416	161.6	87.7	60
	5	1892	161.4	87.9	60
C-C_6H_6	2	207	. . .	. . .	. . .
	3	422	. . .	. . .	. . .
	4	846	. . .	. . .	. . .

4. The Capillary Condensation Theory Modified in Regard to the Critical Condition of Its Inception

The capillary condensation theory is built on the self-evident basis that there are suitable capillary pores in the sorbent. With the so-called porous solid this is unquestionably accepted by everyone. However, the importance of the magnitude of the radius of capillary pores did not appear to be fully appreciated in the past, except in a small circle of researchers, until the B.E.T. equation was extended to cover the whole range of sorption and to show that there were various capillary pores in the porous solid, ranging from molecular crevices to the very large ones. In spite of this situation, it is an undue extension of the capillary condensation theory to say that the sorbate would condense in molecular crevices and the radius of such molecular crevices could be calculated from the vapor pressure by means of the Thomson equation because we cannot form any conception of the surface tension of meniscus for such highly dispersed sorbate and the surface tension is a property of bulk molecular assemblies. In fact, unrestricted application of the Thomson equation gives the absurd result in certain cases that almost all the sorbate would condense in capillary pores smaller than the sorbate molecules. Therefore we have to restrict the applicability of the Thomson equation on a reasonable basis which will be placed by the correct capillary condensation theory. Some years ago, we[8] proposed a critical condition for the limit of applicability of the Thomson equation or for the inception of capillary condensation from thermodynamic considerations, on the basis of assumptions that (1) in a small cluster of molecules or in very small drop, there exerts no surface tension γ, (2) a molecular cluster, grown up to a certain size, may be perceived as a liquid embryo and (3) the surface properties of the dispersed liquid may be exhibited by molecules in the boundary monolayer and they have an excess of the free surface energy per molecule $\gamma\alpha$, where α is the effective area of the molecule in the boundary phase. With these assumptions, he derived a formula $x \equiv P/P_0 \geqq \exp(\pm\gamma\alpha/kT)$, which determines the existence range of dispersed liquid phase. Accordingly, $x_c = P_c/P_0 = \exp(\gamma\alpha/kT)$ is the critical limit for the formation of liquid drop, and

$$x_c = P_c/P_0 = \exp\left(-\frac{\gamma\alpha}{kT}\right) \qquad (1)$$

is the equation of the critical limit for the occurrence of capillary condensation. This critical relative pressure x_c may vary, according to the surface tension γ of the sorbate and the effective area α of the sorbate molecule in the boundary phase of meniscus. However, in general it has a value from 0.2 to 0.4. According to this viewpoint it is unallowable to apply the Thomson equation beyond the critical limit because there exists no liquid phase.

The new capillary condensation theory, taking into account this restriction for applying the Thomson equation, permits the phenomenon to occur in the range of pressure higher than the critical one given by equation (1). On the basis of this theory, the limit of the inception point of hysteresis in isotherms is theoretically given in certain cases where sorbents have favorable pores of rather narrow sizes.

At the critical pressure, the Thomson equation becomes

$$\ln x_c = -(2\gamma M/\rho r_c RT) \qquad (2)$$

where r_c is the critical radius of a cluster of molecules. A cluster with radius greater than r_c may be considered or treated as a dispersed liquid phase. If we take the molecular radius as $r_m = {}^1/_2(M/\rho N)$ from the density of liquid ρ, and the effective area $\alpha = 4r_m^2$, then $\alpha = 4r_m^3/r_m = M/(2\rho N r_m)$. Substituting this into equation (1)

$$\ln x_c = -\frac{\gamma\alpha}{kT} = -\frac{\gamma M}{2\rho r_m N kT} = -\frac{2\gamma M}{4\rho r_m RT}$$

Comparing this equation with equation (2), we can obtain

$$r_c = 4r_m \qquad (3)$$

This indicates that the capillary pore whose radius is twice as large as the molecular dimension is the critical one in which the capillary condensation might occur. Formula (3) is of the same type as that derived by Cohan[9] for the critical limit of hysteresis in isotherms. The present derivation of the formula does not depend on any special assumption on the shape of capillary pore concerned and, basing on the bottle neck pore theory, the lower limit of the hysteresis in isotherms on certain sorbents is given as the limit of occurrence of the capillary condensation. In addition, in this formula, the capillary radius is defined more certainly than that of Cohan as will be described in a later part.

The applicability and the validity of formula (1) have been reported in a number of cases,[1,2] and we shall take this formula as a basis for the following discussions, though the general discussions on this subject shall be postponed to the future.

Higuti[10] obtained the results while working elsewhere that the sorbed amount for completing a monolayer on titania gel which was calculated from the well known B.E.T. plot of the isotherms of various vapors, was found to be near to or slightly less than the amount sorbed at the critical pressure. Therefore, we may state that (according to the B.E.T. plot, adopted as a means of obtaining the surface area experimentally), the monomolecular film has completed and the very small pores, such as molecular crevices, have already been filled up with the sorbate molecules before the capillary condensation is effective, owing to its surface tension which is essential for the vapor pressure depression and for the application of the Thomson equation. Capillary condensation, therefore, except some special cases such as active charcoal–water system, is a phenomenon occurring in pores which have already been covered with the monolayer or the like. Capillary pore size distributions shown in Fig. 3 were obtained according to this view for capillary condensation and therefore radii of capillary pores indicated are not true ones but half intervals between the sorbate molecules forming monolayers on wall of capillary pores, or filling up the molecular crevices. There may be a number of critics against the view adopted here. Such criticism will be discussed in the later paper.

5. The Radius of Pore in Which the Sorbate Would Melt at Temperature Corresponding to the Minimum of $(\Delta T/\Delta t)$–T Curves

According to the capillary condensation theory modified as above, a definite amount of the liquid sorbed at an equilibrium pressure fills up pores of radius (r) smaller than a certain value. If, in addition, the pore structure of the sorbent is known, we can calculate the volume (φ) of the liquid condensing in each capillary pore. One of the authors[4] derived thermodynamically a correlation between the freezing point depression ΔT and the radius of pore, in which the sorbate was condensed, as

$$\frac{\Delta T}{T_0} = \frac{2\gamma M}{\rho r \Delta H} \qquad (4)$$

Here T_0, M and ΔH are the normal melting point, the molecular weight and the heat of fusion for the

---

[9] L. H. Cohan, *J. Am. Chem. Soc.*, **60**, 433 (1938).

[10] I. Higuti, unpublished.

sorbate, respectively, and ρ, γ are the density and the surface tension of the supercooled liquid. Therefore, if the anomalous heat capacities of the sorbate obtained in these experiments are due to melting of the sorbate, condensing in capillary pores the radius of which is determined by the equilibrium pressure according to the Thomson equation it is possible to calculate the relative heat capacity curve $(\Delta T/\Delta t)$-T by taking account of the pore size distribution and the above formula for each of experiments such as shown in Figs. 4, 5 and 6. It is, however, not easy to carry out such computations, because ρ, γ and also ΔH in the above expression are functions of temperature. Hence we shall separate the problem into two lines: (1) what influence the enhanced amount of the sorbate gives to the temperature at which the utmost sorbate would melt, one corresponds to the minimum of curves in Figs. 5 and 6 and then in what pores of radius would the sorbate melt at the temperature? (2) The experimental relation between ΔT and r thus found shall be treated from the theoretical point of view on freezing point depression of the sorbate. If we assume, to a first approximation, ρ, γ and ΔH in equation (4) to be independent of temperature as can be admitted for a comparatively narrow temperature range

$$\mathrm{d}(\Delta T) = -\frac{2\gamma M T_0}{\rho \Delta H} \times \frac{\mathrm{d}r}{r^2} \equiv \alpha \frac{\mathrm{d}r}{r^2}$$

and then

$$\frac{\mathrm{d}\varphi}{\mathrm{d}(\Delta T)} = \frac{\mathrm{d}\varphi}{\mathrm{d}r} \times \frac{\mathrm{d}r}{\mathrm{d}(\Delta T)} = \frac{r^2}{\alpha} \times \frac{\mathrm{d}\varphi}{\mathrm{d}r}$$

The amount of the sorbate melting at T_m with the unit increase of temperature is proportional to $r^2\mathrm{d}\varphi/\mathrm{d}r$, according to the above expression. Therefore if we plot $r^2\mathrm{d}\varphi/\mathrm{d}r$ against r as revealed in curves A′ and B′ in Fig. 3, the radius of capillary pore in which the maximum quantity of sorbate would melt, may be obtained, when the sorbent contains a sufficient amount of the sorbate. From the curve A′, we may assign 60 Å. for the radius of pores in the case of silica gel, but as to the active charcoal, we cannot obtain such a pore characteristic. Then we may conclude, in view of the amount sorbed, that, in the case of silica gel, the sorbate condensing in the pore of radius 60 Å. would melt at the temperatures corresponding to the minima in curves No. 5 and 6 in Fig. 5 and No. 4 and 5 in Fig. 6. However, when the amount of sorbate is less and insufficient to fill the pore of radius 60 Å., the apparent maximum heat capacity must be observed at temperature T_m at which the sorbate filling up the largest pore would melt. This temperature decreases, according to formula (4), as the amount sorbed or the maximum radius of pore filled up decreases. Experimental results exhibited in Figs. 5 and 6 fit this theoretical viewpoint, confirming, although qualitatively, the validity of capillary condensation theory. The cause of slight deviation in experiments with large excess of free liquid will be examined in the later researches.

In the case of active charcoal, similar treatment shows that capillary structure has no remarkably favorable pores in the range concerned and that the amount held in pores of radius less than 20 Å. is 90% of the saturated amount, and in pores of radius less than 38 Å. is 95%. Therefore the amount condensing in pores larger than 38 Å. is very small. We may, therefore, conclude that the absence of the minimum in the curves in Fig. 4, even if the sorbed amount is considerably increased, is due to the capillary structure or pore size distribution of the sorbent. In the last column of Table I, are given such capillary radii of pores calculated from the amount sorbed in each experiment, according to the point of view described in the previous paragraph. In these computations, the value of 60 Å. was obtained, partially on the basis of theoretical formula (4). Other data are, however, computed entirely from experimental results concerned with pore size distribution, obtained by applying the Thomson equation to the isotherm of benzene at 0°. Therefore these values of radii at temperatures corresponding to the maximum heat capacity may be taken as experimental results. In other words, the freezing points of the sorbate condensing in pores of radii indicated in the last column in Table I correspond to the temperatures given in the 4th column.

6. Theoretical Calculation of the Freezing Point Depression of Liquid Condensed in Capillary Pores

In the previous section, it has been shown that the freezing point depression of sorbate is qualitatively in accordance with the capillary condensation theory and the theory for freezing of the sorbate based on it. On the basis of the amount sorbed and the pore size distribution curve, radii of pores were obtained at several temperatures at which the $(\Delta T/\Delta t)$-T curves showed the minimum. In applying formula (4), it was already pointed out[3,4] that, as the density and the surface tension, we could use the values of supercooled liquid. ΔH is the heat of fusion and the value at ordinary melting point may be used for small range of ΔT. However, in a wide range of ΔT, ΔH is not constant and formula (4) loses its validity. In the previous paper,[3] it was pointed out that with the value of ΔH_T at the actual melting temperature, the formula could be applicable even in a large range of ΔT as a practically proper approximation. ΔH_T is easily given by the following thermodynamic relation

$$\frac{\Delta H_T}{T} = \frac{\Delta H_0}{T_0} - \int_T^{T_0} (C_L - C_S)\mathrm{d}\ln T$$

if heat capacities of the solid and liquid phases are determined. We have to resort to this relation, especially in such a case as CCl_4, because solid CCl_4 shows a phase transition at a temperature near the melting point, accompanying a large heat of transition and making it meaningless to adopt the value of ΔH_0, at the bulk melting point. Values of ρ and γ were obtained by extrapolation from those in I.C.T. Necessary values of ΔH_T for benzene were obtained from the work of Huffman, *et al.*,[11] and as for CCl_4, C_S was taken from Latimer's[12] and C_L from Mills' paper.[13] Sub-

---

[11] G. D. Oliver, M. Eaton and H. M. Huffman, *J. Am. Chem. Soc.*, **70**, 1502 (1948).

[12] W. M. Latimer, *ibid.*, **44**, 90 (1922).

[13] J. M. Mills and D. MacRae, THIS JOURNAL, **15**, 54 (1911).

stituting these appropriate values into formula (4), we have ΔT calculated, as shown in Table II.

TABLE II

	Expt. no.	$\Delta T_{\text{obsd.}}$	H_T, kcal./mole	$\Delta T_{\text{calcd.}}$
SiO_2-C_6H_6	2	...	...	(>80)
	3	50.6	1.75	55.2
	4	27.3	2.06	32.0
	5	26.6	2.07	31.4
	6	21.1	2.14	29.8
SiO_2-CCl_4	2	107.7	0.87	129
	3	97.4	0.92	90.7
	4	87.7	1.07	67
	5	87.9	1.07	67

As for benzene, values of ΔH_T thus calculated seem to be more reliable, on account of the accurate determination of C_S and C_L. The agreement between the observed and calculated values of ΔT, however, is not so good as to be expected. Although it is an approximation to take ΔH_T as the latent heat in formula (4), these disagreements might chiefly be attributed to the inaccuracy of these experiments. If we use ΔH_0 for the experiments of No. 4 and 5, the agreement is more desirable. However, it seems to be fortuitous. The greatest deviation, found in No. 6, might be due to some other reason, owing to the presence of a great deal of free liquid of benzene, as stated previously. This anomaly was also found in the case of CCl_4, and will be investigated in the future. ΔT calculated for experiment No. 2, using the necessary physical values at 228.1 °K., is *ca.* 80 °. This value may possibly be increased further and we can understand why the freezing phenomenon was not observed in the range of experimental temperatures. At any rate we can conclude that both the positive and negative results concerned with freezing point depression fit those expected from the theoretical expression. In the case of CCl_4, experimental values of C_S and C_L are not accurate enough to calculate ΔH_T on the basis of those data. Notwithstanding it is not valid at all to use ΔH_0 at normal melting point, on account of the phase transition of solid CCl_4 at $-48°$ accompanying a heat of transition 1.1 kcal. per mole larger than the heat of melting 0.644 kcal. per mole. As represented in Table II, the coincidence is not so favorable, except that of No. 3. In this case, however, ΔH_T is considerably small and ΔT is remarkably large. In addition to these situations, we may take into account the inaccuracy arising from the linear extrapolation of ρ, γ, and especially C_L. According to the lattice model of liquid frequently adopted, linear extrapolation of C_L over the temperature range of 150–270 °K. is not accepted to be strictly valid. On considering many sources of error, we satisfy ourselves with the results obtained in Table II and we can state that, in all cases, indicated in this paper, theoretical formula (4) essentially fits the experimental values for ΔT and that this may be an additional evidence for the capillary condensation theory.

7. Discussion

From the experimental results obtained calorimetrically from three systems indicated above, it has been shown that the sorbate freezes at temperatures lower than the normal melting point and that the freezing point depression ΔT is quantitatively given by the freezing theory of capillary liquid proposed by one of the authors on the basis of the capillary condensation theory.[3,4] He previously evidenced the capillary condensation theory and the freezing theory of the condensate, based on the dielectric property of the sorbate. By means of two lines of experiments, being different in principle of experimental process, we come to the same conclusion. These results seem to lay an unambigous foundation for the capillary condensation theory, which has been obscured by a number of experimental controversies. We can deny some of them at once, but a full discussion may be postponed until sufficient accumulation of our own experimental results. In the previous experiment[2] on freezing of the sorbate, condensing in the capillary pore of radius as narrow as 67 Å., was evidenced and in this experiment the range of the pore size has been reduced to 40 Å. It is of interest and importance to reduce the range as far as possible by the experiment. By this means, the smallest number of molecules to be recognized as liquid phase will be searched for experimentally. In contrast to the success of explaining the experimental results by the capillary condensation theory, other current theories of sorption, for example, the B.E.T. theory of multilayer adsorption cannot stand for these experimental facts. Although we appreciate its usefulness in determining the surface area of powder and its wider applicability as semiempirical formula, its theoretical basis loses validity, especially for sorption phenomena on porous solids. Hitherto many investigators paid too much attention and made remarkable efforts to describe the shapes of the isotherms from the theoretical viewpoint. The B.E.T. theory seems to be the most excellent one ever obtained among them. If even this loses its theoretical validity at least in the case of porous solid, one might turn his view to other lines. According to the authors' opinion, the shape of the isotherms in the high relative pressure range is generally determined by the pore structure of the sorbent, although in the lower relative pressure range, it depends on the area and the nature of the surface. That is the reason why any theoretical formula for the isotherm cannot explain the various experiments in the whole range, even if it is partly successful for some cases. We would say that any attempt to describe the isotherm would not be successful without recognizing the importance of the pore structure of the sorbent, which is very sensitive to the method of preparation and activating conditions. The genuine problem of surface chemistry, dealing with the interaction between the sorbate molecules and the surface might proceed forward, if we would turn our attention to this discrimination of the phenomena. On the other hand, studies on the pore structure of sorbent must be an important subject to be pursued in surface chemistry, bringing the knowledge on the aggregate states of materials.

In conclusion the authors express their cordial thanks to Prof. F. Ishikawa for his helpful advices and encouragement throughout this work. It is also noted that the expense of this research has been defrayed partially from the Grant in Aid for Fundamental Scientific Research.

SOLUBILITIES OF QUATERNARY AMMONIUM SALTS IN CERTAIN ORGANIC SOLVENTS

BY VINCENT L. HUGHES[1] AND ARTHUR A. VERNON

The Hayden Memorial Laboratories, Northeastern University, Boston 15, Massachusetts

Received January 25, 1952

Solubilities are reported for tetramethylammonium iodide and tetrapropylammonium iodide in methanol–benzene mixtures; for tetraethylammonium iodide, tetraethylammonium bromide, tetrapropylammonium iodide and tetrabutylammonium iodide in ethanol–benzene mixtures; for tetraethylammonium iodide and tetrapropylammonium iodide in methanol–nitrobenzene mixtures; for tetraethylammonium bromide, tetrapropylammonium bromide and tetrabutylammonium iodide in ethanol–nitrobenzene mixtures. The ethanol–benzene and ethanol–nitrobenzene solutions all show a maximum in the solubility–mole fraction plot. It is suggested that this may be due to a combination of solute–solvent interaction.

Introduction

Goldberg and Vernon[2] reported the solubility of tetraethylammonium iodide in methanol–benzene mixtures and found that the solubility increased with the mole fraction of methyl alcohol with a maximum value at about 0.8 methanol. Therefore, it was decided to study other solutes and solvent mixtures to determine whether a similar effect was present.

Experimental

Materials.—Tetraethylammonium iodide, prepared by the method reported by Vernon and Sheard,[3] analyzed 49.3% iodine compared to the theoretical value of 49.4%. The other salts were Eastman Kodak materials prepared by recrystallization. Tetramethylammonium iodide was crystallized from a 50% water–methyl alcohol mixture to give an iodine content of 68.1% compared to the theoretical 68.2%.

Tetrapropylammonium iodide was dissolved in hot methyl alcohol, the solution cooled for crystallization, and precipitation completed by the addition of ether. The salt was dried at 70° to give an iodine content of 40.4% compared to the theoretical 40.5%.

Tetrabutylammonium iodide was crystallized from benzene and dried in a vacuum desiccator to give an iodine analysis of 34.4% compared to the theoretical 34.3%. Tetraethylammonium bromide was crystallized from absolute ethyl alcohol and dried in a vacuum oven at 70°. The salt analyzed 38.1% bromine compared to the theoretical 38.1%.

Anhydrous methyl alcohol and benzene were purified as described by Goldberg and Vernon.[2] The methyl alcohol had a refractive index of 1.3271 at 25° compared to the "International Critical Tables" value of 1.32773. The benzene refractive index was 1.4977 at 25° compared to the "International Critical Tables" value of 1.49779.

95% ethyl alcohol was refluxed and distilled off calcium oxide and in turn off silver oxide. The solvent was then dried over calcium hydride and distilled.

Nitrobenzene was shaken with sulfuric acid and then with sodium carbonate solution. After a further shaking with distilled water, the solvent was stored over activated alumina for three days, filtered and stored over calcium hydride for two weeks.

Procedure.—The method of saturation and solution removal was the same as that described by Goldberg and Vernon.[2] The analyses of the methanol–benzene solutions were made by a modified Volhard analysis as described by the same authors. The solutions containing nitrobenzene were usually analyzed by adding ethyl alcohol, titrating with silver nitrate, and digesting on a steam-bath for 20 minutes. After adding an equal volume of hot distilled water, the precipitate settled to leave a clear supernatant liquid. Further titrations could be performed to a sharp end-point.

Results

The results of the measurements are plotted in Figs. 1, 2, 3 and 4 in which the solubility values are the averages of from three to five determinations. Eight of the values of solubility have average deviations from the mean from 1 to 1.5%; the rest are considerably less than 1%.

Discussion

The additional data obtained for the solvent pair methanol–benzene do not lead to a consistent behavior when added to the information reported by Goldberg and Vernon.[2] If the maximum is due to methanol interaction with the iodide ions, it would seem that the effect should be more pronounced for the tetrapropylammonium iodide since the large cation should favor anion–methanol interaction.

The ethanol–benzene and ethanol–nitrobenzene curves present a more consistent picture although it seems evident that other studies than solubility would have to be made to establish a theoretical explanation of the behavior found. However, the following comments seem justified as a preliminary proposal. The behavior of the solute is approximately the same in both liquid pairs with the maximum lying between methanol mole fractions of 0.7 and 0.85. It is interesting that in ethanol–benzene both tetraethylammonium iodide and tetraethylammonium bromide show a maximum since Goldberg and Vernon[2] found that tetraethylammonium bromide gave no maximum in methanol–benzene mixtures.

Copenhafer and Kraus[4] showed that many quaternary ammonium salts are highly associated in benzene solutions. Further, they found that the association numbers went through a maximum at different concentrations for different salts—usually between about 0.1 and 0.3 molal. If such an effect were the cause of the behavior in the systems here reported it would be likely that the association would be decreased by increase in dielectric constant and if such decrease took place, the solubility should drop. However, it is doubtful if this can be the cause of the solubility behavior since maxima are more consistently obtained with ethanol than with methanol which has the higher dielectric constant of the two alcohols.

---

(1) Clark University, Worcester, Massachusetts.

(2) G. M. Goldberg and A. A. Vernon, *J. Am. Chem. Soc.*, **73**, 2845 (1951).

(3) A. A. Vernon and J. L. Sheard, *ibid.*, **70**, 2035 (1948).

(4) D. T. Copenhafer and C. A. Kraus, *ibid.*, **73**, 4557 (1951).

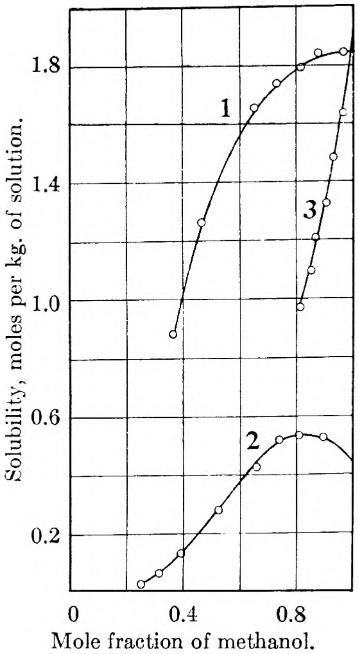


Fig. 1.—Solubility in methanol-benzene mixtures: 1, tetramethylammonium iodide × 10^2; 2, tetraethylammonium iodide from Goldberg and Vernon; 3, tetrapropylammonium iodide.

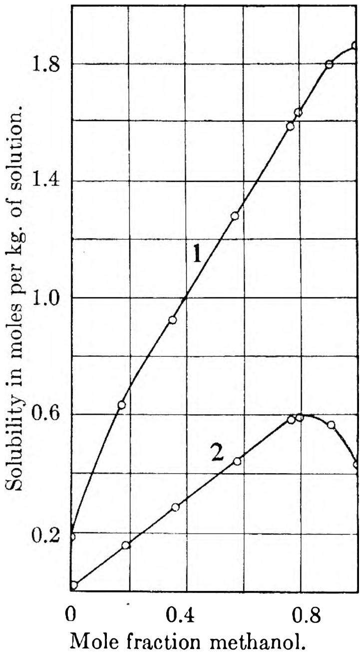


Fig. 3.—Solubility in methanol-nitrobenzene mixtures: 1, tetrapropylammonium iodide; 2, tetraethylammonium iodide.

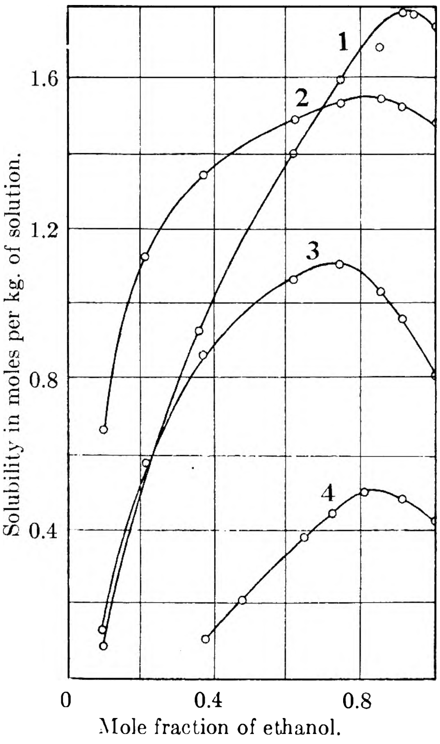


Fig. 2.—Solubility in ethanol-benzene mixtures at 25°: 1, tetraethylammonium bromide; 2, tetrabutylammonium iodide; 3, tetrapropylammonium iodide; 4, tetraethylammonium iodide × 10.

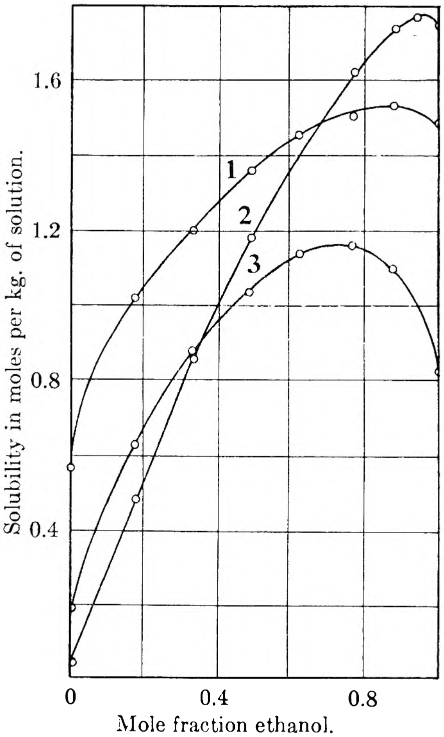


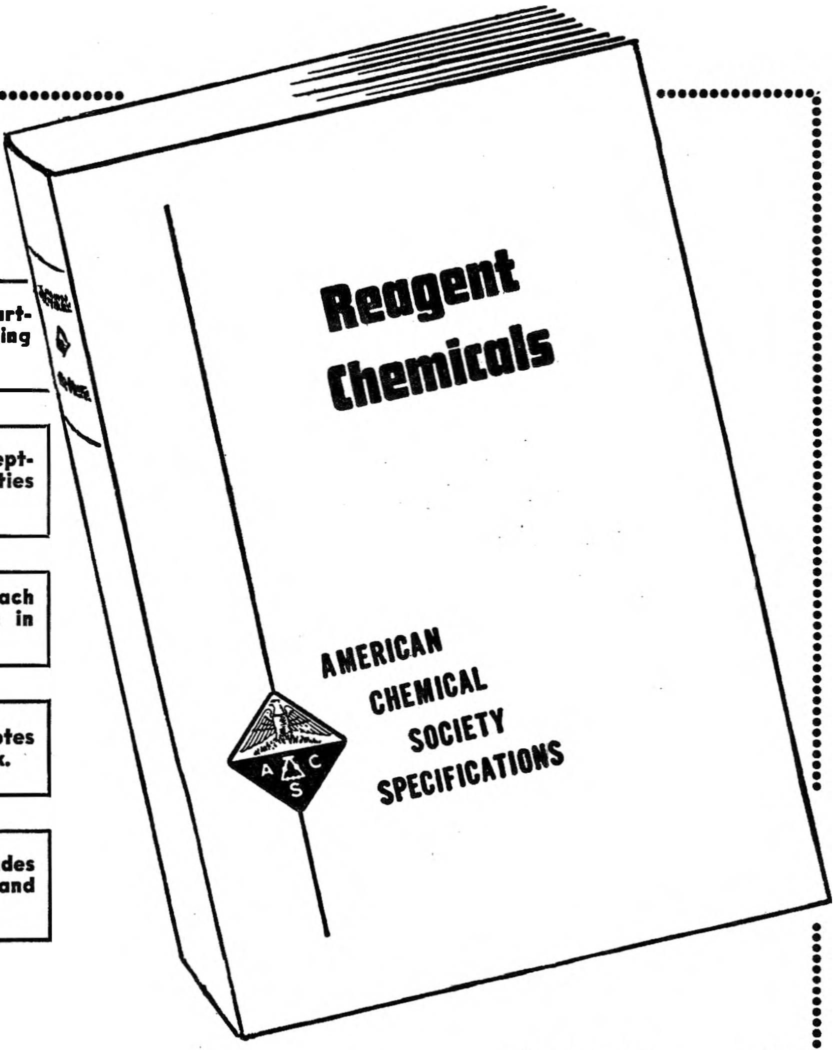
Fig. 4.—Solubility in ethanol-nitrobenzene mixtures at 25°: 1, tetraethylammonium bromide; 2, tetrabutylammonium iodide; 3, tetrapropylammonium iodide.

Sadek and Fuoss[5] cited evidence of solvent-solute interaction with tetrabutylammonium bromide in methanol-nitrobenzene mixtures. It seems likely that such effects are present in the systems here reported. Apparently the nitrobenzene negative dipole interaction is less important than the ethanol dipole interaction since the ethanol-nitrobenzene curves are not greatly different from the ethanol-benzene curves. The ethanol interaction seems to be stronger than the methanol interaction since maxima are more predominate with ethanol-benzene mixtures than with those of methanol-benzene.

The authors express their appreciation to the Research Corporation which supported this work.

---

(5) H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950).


Reagent Chemicals
AMERICAN CHEMICAL SOCIETY SPECIFICATIONS
A C S