Statistical Theory of Chemical Reaction Rates*

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A "statistical" theory of chemical reaction rates based on "scattering theory" in the strong coupling approximation is presented. The theory is developed explicitly for reactions involving the dissociation and recombination of a diatomic molecule in the presence of an atomic catalyst but is also readily applicable to other reactions. The theory formally includes Wigner's theory of three-body recombination and the classical theories of both recombination and dissociation. A limited comparison with experiment shows reasonable agreement.

INTRODUCTION

IN the present paper we should like to propose a "statistical" theory of chemical reaction rates applicable to processes involving strong interactions which cannot be handled by existing techniques. The theory is based on "scattering theory" in the strong coupling approximation[1] and involves the calculation of that part of the reaction rate governed by the purely statistical phase space factors. Thus by comparing theory and experiment we can expect to obtain directly useful information about the detailed transition probabilities for a reaction.

Although the theory is formally applicable to any chemical reaction, it will be developed explicitly only for dissociation and recombination of a diatomic molecule by collision with an atomic catalyst. An important feature of the theory as applied to these reactions is that it establishes a connection between the "three-body collision" theories of recombination[2-4], the "available energy" theories of dissociation,[5-9] and the Wigner theory of recombination.[10] These theories, which previously appeared to give conflicting results, are found to be special cases of the more general "statistical" theory, each valid under a clearly defined set of assumptions and appropriate in different temperature ranges.

Our primary concern in the present paper will be in communicating the fundamental ideas of the theory and discussing their relation to previous theoretical work. For this reason the notation employed is extremely concise and intended mainly to illustrate the

form in which the results are obtained. Also the comparison with theory is made only for the case of iodine atoms recombining in the presence of noble gases. A second paper is in preparation which will give the details of the calculations and make comparison with all available experimental data.

GENERAL DEVELOPMENT

The process we wish to consider is represented by the chemical equation,

$$A+B+C \rightleftharpoons AB+C. \qquad (1)$$
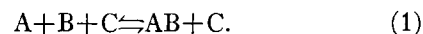
The reaction proceeding to the right represents the recombination of two atoms, A and B, in a collision in which a third atom, C, carries away the energy released; that proceeding to the left represents the dissociation of a molecule, AB, in a collision in which an atom, C, supplies the energy required. For simplicity we assume that the interaction of C with either A or B is repulsive so that no other reactions are possible. We further assume that the probability of an electronic transition during a collision is negligible so that the interaction potential for the system can be uniquely specified. Although generalization of the theory to include both attractive interactions with C and electronic transitions is relatively simple, the case considered is, in practice, the most important since, even for a "reactive" catalyst, the large majority of electronic configurations lead to repulsive interactions and the collisions are expected to be adiabatic as far as the electrons are concerned. The collisions will be treated in the classical approximation. The justification for this is that (1) the deBroglie wavelength of the interacting atoms is often small compared to the ranges of the forces involved so that a description of the collision in terms of particle trajectories is meaningful, (2) the energy transfer involved in changing the chemical state of a molecule is, in general, large compared to the spacing of molecular rotation and vibration levels so that many quantum states are involved, and (3) we shall ultimately be concerned only with counting the number of quantum states compatible with certain

[1] See, e.g., J. M. Blatt, and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952).
[2] W. Steiner, Z. physik. Chem. (Leipzig) B15, 249 (1932).
[3] E. Rabinowitch, Trans. Faraday Soc. 33, 283 (1937).
[4] B. Lewis and G. von Elbe, Chem. Revs. 21, 349 (1937).
[5] R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Cambridge University Press, New York, 1952).
[6] O. K. Rice, J. Chem. Phys. 9, 258 (1941); 21, 750 (1953).
[7] G. Careri, J. Chem. Phys. 21, 749 (1953).
[8] H. Bethe and E. Teller, BRL Report X–117.
[9] J. G. Logan, Jr., IAS Preprint No. 728 (1957).
[10] E. P. Wigner, J. Chem. Phys. 5, 720 (1937); 7, 646 (1939).

restrictions, and this may be done classically to sufficient accuracy for our purposes even when only a few states are involved. An advantage of classical mechanics over quantum mechanics is that both the position and momentum of an atom can be specified without using wave packets and this permits us to define a collision in simpler terms.

In accord with generally accepted principles we assume that the over-all reaction in either direction can be described by the motion of a point in the 18-dimensional phase space of three particles from the initial chemical state through a "collision complex" to the final chemical state. It is usually loosely stated that the "collision complex" is entered from the "free" state, $A+B+C$, as a result of a three-body collision and from the "bound" state, $AB+C$, as a result of a "two-body" collision. It should be noted however that the "two-body" collisions actually involve *three* particles so that it is more precise to say that the formation of the "collision complex" is always the result of a three-body collision. Since there may be some confusion as to the definition of a three-body collision, we shall define it, for our purposes, as the collision of a third particle with any pair of interacting particles regardless of their internal state of motion. If the potentials characterizing the interactions between the atoms are sharply cut off, as they are for chemical bonds, the boundaries of the "collision complex" can be located with relatively little uncertainty by specifying the value of the potential at which an effective interaction is assumed to occur. The essential point to keep in mind is that outside the "collision complex" the equations of motion should be separable in terms of a free atom and a molecule or three free atoms while inside all three particles should be strongly coupled. As a result of the above definition there are six ways for a three-body collision to occur in the "free" state and two ways for it to occur in the "bound" state. This is the only important difference between "two-body" and "three-body" collisions as applied to the reactions considered.

We shall treat first the recombination reaction and then the dissociation reaction. To obtain an expression for the recombination rate, $\Re_{fb}$, we consider the steady-state flow of representative points in phase space from the "free" state through the "collision complex" to the "bound" state. This flow is restricted by conservation laws to "shells" on which the total linear momentum, $\mathbf{P}$, the total angular momentum, $\mathbf{L}$, and the total energy, E, are constant. The recombination rate may, therefore, be written in the form:

$$\Re_{fb} = \iiint_{R_f \epsilon_{fb} > 0} R_f(\mathbf{P}LE)\epsilon_{fb}(\mathbf{P}LE)d\mathbf{P}dLdE, \quad (2)$$

where $R_f(\mathbf{P}LE)$ is the collision rate in the "free" state for systems of fixed $\mathbf{P}$, $\mathbf{L}$, and E and $\epsilon_{fb}(\mathbf{P}LE)$

is the corresponding recombination probability. Since R_f can be calculated in accord with the discussion above, our problem is to estimate ϵ_{fb}.

At the present time, the possibility of making an exact calculation of ϵ_{fb} appears remote. First, the required three-body interaction potential is not known nor have we adequate methods for calculating it. Second, even if we assume the potential known, we still have no method for solving the general three-body problem. Some attempts have been made to apply perturbation theory to the problem, but since strong forces are clearly involved in the reaction, the approach is difficult to justify and has not proved fruitful.[11] The problem might be handled by a modern high-speed computer but exploratory calculations of this type have shown that the trajectories are often of exquisite complexity and this does not appear attractive.

In view of this rather discouraging situation, we should like to propose a statistical approach to the problem of estimating ϵ_{fb}. Our fundamental assumption is that the collisions are sufficiently complicated to establish an equilibrium distribution of systems leaving the "collision complex." To put it more precisely, we assume that, subject to known conservation laws, the density in phase space of systems leaving the "collision complex" is uniform, independent of the initial density of systems entering. As a consequence, the recombination probability can be written:

$$\epsilon_{fb}(\mathbf{P}LE) = \Gamma_b(\mathbf{P}LE)/[\Gamma_f(\mathbf{P}LE)+\Gamma_b(\mathbf{P}LE)], \quad (3)$$

where $\Gamma_b(\mathbf{P}LE)$ and $\Gamma_f(\mathbf{P}LE)$ are the rates of flow of phase volume per unit $\mathbf{P}$, $\mathbf{L}$, and E across the boundaries of the "collision complex" to the "bound" and "free" states, respectively. R_f may be expressed in terms of Γ_f by the equation,

$$R_f(\mathbf{P}LE) = \rho_f(\mathbf{P}LE)\Gamma_f(\mathbf{P}LE), \quad (4)$$

where $\rho_f(\mathbf{P}LE)$ is the density in phase space of systems colliding in the "free" state with fixed $\mathbf{P}$, $\mathbf{L}$, and E. Combining Eqs. (2), (3), and (4), we obtain the recombination rate in the form,

$$\Re_{fb} = \iiint_{\rho_f\Gamma_f\Gamma_b > 0} \rho_f\frac{\Gamma_f\Gamma_b}{\Gamma_f+\Gamma_b}d\mathbf{P}dLdE. \quad (5)$$

Γ_b and Γ_f can be expressed explicitly as integrals in the form,

$$\Gamma_b = \int_{\lambda_b} |\mathbf{V}\cdot\mathbf{n}| d\lambda, \quad (6a)$$

and

$$\Gamma_f = \int_{\lambda_f} |\mathbf{V}\cdot\mathbf{n}| d\lambda, \quad (6b)$$

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[11] E. Bauer, Phys. Rev. **84**, 315 (1951); **85**, 277 (1952).

where $\mathbf{V}$ is the generalized velocity of a point in phase space, $\mathbf{n}$ is the unit normal to a 17-dimensional "surface" element, $d\sigma$, of the "collision complex," and $d\lambda$ is related to $d\sigma$ by the equation,

$$d\sigma = d\lambda dPdLdE. \qquad (7)$$

The integration is to be carried out over the 10-dimensional "lines" $\lambda_b(PLE)$ and $\lambda_f(PLE)$ involved in defining the appropriate boundaries of the "collision complex."

The same line of argument followed in the derivation of the recombination rate may be used to derive the dissociation rate, $\mathfrak{R}_{bf}$, and leads to an expression similar to Eq. (5) in which the subscripts f and b are simply interchanged,

$$\mathfrak{R}_{bf} = \underset{\rho_b\Gamma_b\Gamma_f>0}{\iiint} \rho_b \frac{\Gamma_b\Gamma_f}{\Gamma_b+\Gamma_f} dPdLdE. \qquad (8)$$

Generalization of Eqs. (5) and (8) to include the possibility of an attractive catalyst can be accomplished by replacing Γ_b in the denominator, $(\Gamma_f+\Gamma_b)$, by a sum over all bound chemical states.

In concluding this section we note that in addition to the constraints imposed by the rigorous conservation laws, it may be physically reasonable in certain cases to restrict other variables. For example, in a collision involving a repulsive catalyst the collision time may be so short that the relative positions of the particles can be regarded as approximately conserved. Such approximate conservation laws can be handled in exactly the same manner as the rigorous laws.

RATES AT EQUILIBRIUM

Although Eqs. (5) and (8) can be applied to non-equilibrium situations, we shall confine the discussions in the remainder of this paper to the case where the distribution of systems is given by the equilibrium Boltzmann distribution,

$$\rho_f{}^e = \rho_b{}^e = \theta e^{-E/kT}. \qquad (9)$$

The constant, θ, may be written either

$$\theta = [A][B][C]/Q_f \qquad (10a)$$

or

$$\theta = [AB][C]/Q_b, \qquad (10b)$$

where Q_f and Q_b are respectively the classical partition functions for the "free" and "bound" states and the brackets, [ ], are used to denote particle concentrations. It follows on inserting Eq. (9) into Eqs. (5) and

(8) that:

$$\mathfrak{R}_{fb} = \mathfrak{R}_{bf} = \theta \underset{\Gamma_f\Gamma_b>0}{\iiint} e^{-E/kT} \frac{\Gamma_f\Gamma_b}{\Gamma_f+\Gamma_b} dPdLdE. \qquad (11)$$

Since the first equality represents a necessary condition at equilibrium the theory is seen to be self-consistent.

The rate constants for recombination and dissociation are defined respectively by the equations,

$$k_R = \mathfrak{R}_{fb}/[A][B][C], \qquad (12a)$$

and

$$k_D = \mathfrak{R}_{bf}/[AB][C]. \qquad (12b)$$

As a consequence of these definitions and Eq. (11), we find that $k_D = k_R K_c$, where $K_c = [A][B]/[AB]$ is the equilibrium constant for the reaction.

LIMITING EXPRESSIONS FOR THE REACTION RATE

It is of considerable interest to investigate Eq. (11) for the equilibrium reaction rate in three special cases where it reduces to expressions previously proposed and in current use.

The first case is that in which the temperature energy is much smaller than the binding energy of AB, i.e., $kT/D\ll1$. Under these circumstances we may reasonably expect Γ_b to be much larger than Γ_f so that it will be a good approximation to set the factor

$$\Gamma_b/(\Gamma_f+\Gamma_b)$$

equal to unity. This is equivalent to the assumption that every three-body collision results in recombination and reduces Eq. (11) to the ordinary "three-body collision" rate, $\mathfrak{R}_3$:

$$\mathfrak{R}_{fb} = \mathfrak{R}_{bf} \rightarrow \mathfrak{R}_3 = \theta \underset{\Gamma_f\Gamma_b>0}{\iiint} e^{-E/kT}\Gamma_f dPdLdE : \frac{kT}{D} \rightarrow 0. \qquad (13)$$

Implicit in this treatment is the assumption that the interaction potentials are sharply cut off so that the effects of weak interactions associated with the "tails" of the potential curves are confined to a small region of configuration space and may be neglected. This is almost certainly true for the strong chemical bond but is questionable for the Van der Waals force. Among the investigators who have taken this approach to the problem are Steiner,[2] Rabinowitch,[3] and Lewis and Van Elbe.[4]

The second case is that in which the temperature energy is much greater than the binding energy of AB, i.e., $kT/D\gg1$. In this case we may reasonably expect Γ_f to be larger than Γ_b so that it will be a good

approximation to set the factor $\Gamma_f/(\Gamma_f+\Gamma_b)$ equal to unity. This is equivalent to the assumption that every "two-body" collision in which the energy is available results in dissociation and reduces Eq. (11) to what we shall call the "available energy" rate, $\mathcal{R}_A$,

$$\mathcal{R}_{fb}=\mathcal{R}_{bf}\rightarrow\mathcal{R}_A=\theta\iiint_{\Gamma_f\Gamma_b>0} e^{-E/kT}\Gamma d\mathbf{P}d\mathbf{L}dE:\frac{kT}{D}\rightarrow\infty. \quad (14)$$

The reaction has been considered from this point of view by Fowler and Guggenheim,[5] Rice,[6] Careri,[7] Bethe and Teller,[8] and Logan.[9] It is fairly clear that $\mathcal{R}_A$ is a poor approximation to the reaction rate at temperatures ordinarily of interest where $kT<D$. Various procedures have been used for estimating the number of "effective" collisions but none of them has been precisely formulated.

The final case involves a calculation by Wigner[10] of a rigorous upper bound to the recombination rate. Wigner observed that a necessary condition for recombination is that the relative energy, $H_0=p_{12}/2m_r+V(r_{12})$, of the reacting pair of atoms be depressed below the value $H_0=0$.[†] To obtain the Wigner result from our present theory we consider the reaction in the low-temperature limit and set the factor $\Gamma_b/(\Gamma_f+\Gamma_b)$ in Eq. (11) equal to unity. Thus the possibility of redissociation in a single collision is ignored and Eq. (11) reduces to the three-body collision rate given in Eq. (13). Next we define an "effective" three-body collision as one in which the system crosses the surfaces $H_0=0$ from above and observe that the unit outward normal, $\mathbf{n}$, to this surface may be expressed as

$$\mathbf{n}=\nabla H_0/|\nabla H_0|. \quad (15)$$

Combining Eqs. (6b), (7), (13), and (15), we obtain

$$\mathcal{R}_w=\theta\int_{\substack{(\mathbf{V}\cdot\nabla H_0)<0\\H_0=0}} e^{-E/kT}\frac{|\mathbf{V}\cdot\nabla H_0|}{|\nabla H_0|}d\sigma$$

$$=-\theta\int_{\substack{dH_0/dt<0\\H_0=0}} e^{-E/kT}\frac{(dH_0/dt)}{|\nabla H_0|}d\sigma. \quad (16)$$

Since our E is the same as Wigner's H this is precisely the Wigner result. It is worth noting that while the surface $H_0=0$ is defined for all configurations of our three particles, the density of trajectories crossing $H_0=0$ will be appreciable only on that portion which

lies inside the "collision complex." This is a simple consequence of the fact that H_0 is a constant of the motion unless there is an interaction with a third body. The conditions under which the Wigner theory is a good approximation will be discussed in the following section.

The only remaining theory which we have not yet considered is that developed by Eyring and his collaborators[12] primarily for dealing with metathetic (exchange) reactions. In the Eyring theory an attempt is made to solve the exact mechanics of the collisions after imposing suitable constraints upon the motion. As applied to reactions involving dissociation or recombination (where a linear complex is usually assumed), these constraints are artificial and lead to the prediction of a recombination rate constant which possesses a minimum and diverges at both low and high temperatures.[‡] If the constraints are removed the Eyring theory reduces to a "three-body collision" theory but the ability to calculate the transmission coefficient is lost.

In concluding this discussion we should like to emphasize that for a given potential each of the rates given by Eqs. (13), (14), and (16) constitutes a valid *upper bound* to the reaction rate. Although, strictly speaking, only the Wigner result can be regarded as "rigorous," in actual practice they can all be defined with about the same precision and are equally good. For any set of conditions, that bound which lies lowest will be the best approximation to the true reaction rate.

RECOMBINATION RATE OF IODINE

Although we do not propose to go into the details of how one calculates the various integrals involved in our expressions for the reaction rates, we should like to present just a few numerical results which will give the reader some idea of how the various theories compare with each other and with experiment. The case considered is the recombination of two iodine atoms in the presence of an argon atom to form the ground state of the iodine molecule. All the calculations were carried out for a Morse potential interaction between the iodine atoms,[13] and integrals over their relative separation were cut off at the point where the magnitude of the potential was approximately kT. Thus the effect of decreasing cross section with increasing temperature has been partly taken into account. The interaction distance between an iodine atom and the catalyst was taken to be the sum of their kinetic theory radii at

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[†] An alternative also considered by Wigner is to calculate the rate at which the relative energy H_0 is depressed below the rotational barrier. In the opinion of the author this case is worthy of further investigation.

[12] Eyring, Gershinowitz, and Sun, J. Chem. Phys. **3**, 786 (1935). See also Glasstone, Laidler, and Ehring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).
[‡] We have assumed the transmission coefficient is insensitive to temperature variation.
[13] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951).
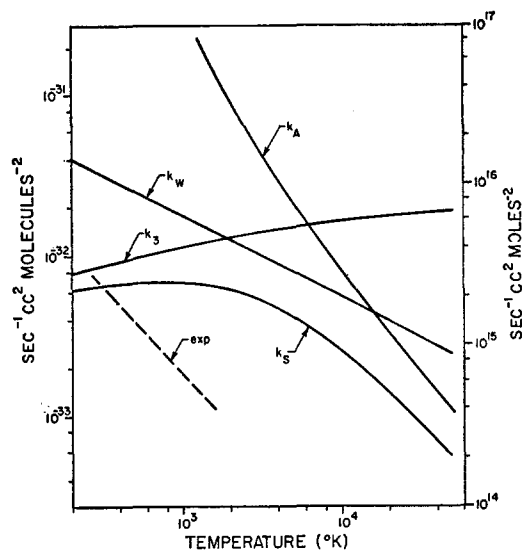
FIG. 1. Recombination rate constants for the reaction $I+I+A \rightarrow I_2(\Sigma_g^+)+A$ as a function of temperature. The curves show the results for the "statistical" theory, k_s, the "three-body collision" theory, k_3, the Wigner theory, k_w, and the "available energy" theory, k_A. In the text it is shown that the latter three theories are special cases of the former and each gives an upper bound to the rate constant. The dashed curve represents the experimental data as summarized by Bunker and Davidson.[15] The comparison of theory and experiment is discussed in the text.

room temperature.[14] This is certainly a poor approximation at high temperatures which could easily lead to an overestimate of the rate by a factor of 2. It was also assumed that no change in electronic state occurs during a collision, and a factor of 1/16 equal to the degeneracy of the ground state divided by the degeneracy of two $^2P_{3/2}$ atoms, has been included where appropriate.

The calculated recombination rate constants are shown as a function of temperature in Fig. 1. The curve marked k_s is the "statistical" rate constant. It has a maximum in the neighborhood of 700°K. At low temperatures it is proportional to $T^{1/3}$ and is asymptotic to the "three-body collision" curve marked k_3; at high temperatures it is proportional to T^{-1} and is asymptotic to the "available energy" curve marked k_A. The Wigner rate constant is given by the curve marked k_W and is everywhere proportional to $T^{-1/2}$. At low temperatures the Wigner rate exceeds the "three-body" rate and is therefore a poor upper bound. At intermediate temperatures the Wigner rate lies below both the "three-body" and "available energy" rates and is, therefore, a better upper bound. At high temperatures the Wigner rate exceeds the "available energy" rate and is again a poor upper bound.

Although the "statistical" rate must lie below the "three-body" and "available energy" bounds, there is

[14] Christie, Norrish, and Porter, Proc. Roy. Soc. (London) A216, 152 (1953).

no a priori reason for it to lie below the Wigner bound. If it does, it is probably a better approximation to the true rate. If it does not, we can improve it by a generalization which includes the Wigner criterion explicitly. In this generalization the reaction is viewed as a three-step process involving: (1) entry into the "collision complex," (2) passage through the surface $H_0=0$, and (3) exit from the "collision complex." Making our statistical assumption at each step leads to a reaction rate of the form,

$$\mathfrak{R}_{fb}=\mathfrak{R}_{bf}=\theta \iiint e^{-E/kT} \frac{\Gamma_f \Gamma_w \Gamma_b}{\Gamma_f \Gamma_w+\Gamma_f \Gamma_b+\Gamma_w \Gamma_b} d\mathbf{P} d\mathbf{L} dE,$$

(17)

which must lie beneath all bounds.

The experimental results on the temperature dependence of the iodine recombination rate have been summarized by Bunker and Davidson[15] and are represented in Fig. 1 by the dashed curve. There are two points which we should like to make from the comparison of theory and experiment. First, since the experimental curve lies below the theoretically predicted upper bounds by a relatively small factor, the strong coupling approach is reasonable. Second, since the experimental rate constant decreases with temperature more rapidly than the theoretical prediction, the detailed mechanics of the collision does influence the reaction rate. In a general way the discrepancy can be explained by assuming a decrease in transition probability with increasing energy. This is a very reasonable thing to expect.

A further comparison of theory with experiment is made in Table I which gives the dependence of the rate constant on the mass of noble gas catalysts. The experimental data are those of Christie, Norrish, and Porter[14] and Russell and Simons.[16] Both theory and experiment have been normalized to unit rate constant for a helium catalyst. Here the agreement is reasonably good. However, before a proper evaluation of the use-

TABLE I. Comparison of theoretical and experimental rate constants for recombination of iodine atoms by noble gas catalysts at 300°K. The rate constants have been normalized to unity for helium. The experimental data are those of Christie, Norrish, and Porter[14] and Russell and Simonds.[16]

Catalyst	He	Ne	A	Xe	Kr
Stat. Theo.	1	1.21	1.7	1.8	1.9
Exp.-CNP	1	1.07	1.39	1.95	1.97
Exp.-RS	1	1.06	2.12	...	...

[15] D. L. Bunker and Norman Davidson, California Institute of Technology, Department of Chemistry TR II-2 (February, 1958).
[16] K. E. Russell and J. Simons, Proc. Roy. Soc. (London) A217, 217 (1953).

fulness of the theory can be made, a more careful and comprehensive comparison with all available experimental material must be made. This is in preparation.

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Sedimentation in Multicomponent Systems

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The formalism of irreversible thermodynamics is employed to derive expressions for the sedimentation coefficients of the species in a multicomponent system in terms of experimentally accessible quantities. Equations are presented for certain limiting cases which may be encountered experimentally. The determination of the hydration of macromolecules by sedimentation methods is examined.

INTRODUCTION

SEDIMENTATION velocity studies have proved to be an extremely valuable means of investigating the heterogeneity of macromolecular solutions and a convenient method for the determination of molecular weights when coupled with diffusion studies. The Svedberg equation has been employed in the interpretation of data from almost all systems investigated even though the original reasoning which led to this equation was plainly limited to binary solutions.[1] In practice most measurements are necessarily made on solutions of more than two components. This has led to attempts at semiempirical modification of the Svedberg equation[2] and to generalizations of the original treatment with the view of obtaining expressions suitable for multicomponent systems.[3]

De Groot and co-workers[4] have in the past few years discussed the application of irreversible thermodynamics to sedimentation processes and have presented a derivation of the Svedberg equation for binary solutions.[5] Hooyman has quite recently extended this treatment to multicomponent systems and em-

ployed his equations to explain certain boundary phenomena observed in ternary systems.[6]

In this work we shall utilize the general approach of irreversible thermodynamics which yields expressions for the sedimentation coefficients of the species in multicomponent solutions involving only directly measurable quantities. The results so obtained allow certain connections with equilibrium measurements on these systems, *viz.*, light scattering and equilibrium dialysis.

Phenomenological Equations

We begin with the set of phenomenological equations for the fluxes in terms of the forces for an n component system. The following treatment will be most directly applicable to a system of nonelectrolytes. It presumably can be extended to a solution of electrolytes by employing a suitable definition of electrically neutral components as has been proposed in treatments of diffusion.[7] The n fluxes $\mathbf{J}_i$ (moles per unit area per unit time) are expressed as a linear combination of the n generalized forces $\mathbf{X}_k$.

$$\mathbf{J}_i = \sum_{k=1}^{n} L_{ik} \mathbf{X}_k \qquad (1)$$

The n^2 quantities L_{ik} are the phenomenological coefficients for the set of fluxes and forces. The fluxes are

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* Present address.

[1] See T. Svedberg and K. O. Pederson, *The Ultracentrifuge* (Clarendon Press, Oxford, 1940), p. 5.

[2] H. K. Schachman and M. A. Lauffer, J. Am. Chem. Soc. **72**, 4266 (1950).

[3] A. G. Ogston, Trans. Faraday Soc. **50**, 1363 (1954).

[4] de Groot, Mazur, and Overbeek, J. Chem. Phys. **20**, 1825 (1950).

[5] Hooyman, Holtan, Mazur, and de Groot, Physica **19**, 1095 (1953).

[6] G. J. Hooyman, Physica **22**, 761 (1956).

[7] B. R. Sundheim, J. Chem. Phys. **27**, 791 (1957).