

Macroscopic and Microscopic Restrictions on Chemical Kinetics

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I. Introduction

The idea that specific restrictions upon the equations of chemical kinetics do, in fact, exist, is generally accepted, even though a well-known text on chemical kinetics by Frost and Pearson¹ expresses the opinion that the relationship between the rate constants and the equilibrium constant might be "... any function, for that matter, and still be consistent".

A rudimentary treatment of the thermodynamic restrictions upon chemical kinetics is often included in elementary texts, somewhat as follows; consider the chemical reaction



where a , b , c , d , are the mole numbers of A, B, C, D, respectively. Further, suppose that the rate of reaction is given by

$$\begin{aligned} -\frac{1}{a} \frac{d[A]}{dt} &= -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \\ &= k_f[A]^a[B]^b - k_r[C]^c[D]^d \quad (2) \end{aligned}$$

and that an equilibrium constant exists as defined by

$$K = ([C]^c[D]^d/[A]^a[B]^b)_{\text{equil}} \quad (3)$$

Then, at equilibrium, the rate must vanish, and eq 2 and eq 3 then give

$$k_f/k_r = ([C]^c[D]^d/[A]^a[B]^b)_{\text{equil}} = K \quad (4)$$

Equation 4 is a form of the rate quotient law, which was here derived in a grossly oversimplified fashion; however, the crucial features of the origin of thermodynamic restrictions upon chemical kinetics *are* apparent here. First, rate constants and thermodynamic equilibrium constants are functions of temperature only; in particular, they are independent of time and of chemical composition (portability property). Second, the equilibrium state of a given system is a unique state, independent of the particular language used to describe it; in the present context, this implies that the rate (eq 2) vanishes if, and only if, the thermodynamic conditions for equilibrium (eq 3) are satisfied.

Section II of the present review is concerned with a general investigation of the consequences of these two macroscopic, empirical principles, wherein the rate quotient law appears as a simple special case; a major portion of this section of the article has already been covered in an elegant fashion by Denbigh.² However, Denbigh's treatment² does not comprise a complete coverage of the literature, and some additional useful results are included here.

It is well known that microscopic considerations enter into chemical kinetics as a consequence of the physical principle of microscopic reversibility; the best known work in this regard is that of Onsager,³ who demonstrated the relationship between microscopic reversibility and the chemist's empirical principle of detailed balance as applied to elementary chemical reactions.

Section III of the present work is devoted to a more detailed examination of this aspect, in the light of more modern theories of chemical kinetics. However, since the principle of detailed balance is used in the derivation of certain results properly included in part II, this portion also includes a definition of this principle as used in the present work, and an indication of exactly where it ceases to be an empirical, macroscopic result, and requires microscopic justification.

In section IV, examples drawn from the literature are used to illustrate both the meaning and usefulness of the principles described earlier. The examples used reflect the particular interests of the writer, but it is hoped that they are sufficiently diverse to clarify the rather abstract discussion in sections II and III.

The present work is, unavoidably, largely mathematical in nature, although the mathematics involved are fairly elementary

and should be familiar to anyone who has been exposed to a medium-level treatment of quantum chemistry. An attempt has been made to keep the mathematics in the main text to a minimum, by relegating some of the lengthier derivations to the Appendix. In this way, it is hoped that the physical and chemical meaning of the treatment described here will at all times be in the forefront of the reader's attention.

II. Thermodynamic Restrictions

This section is chiefly concerned with the general consequences for chemical kinetics of the uniqueness of the equilibrium state, independent of whether this state is described in thermodynamic or kinetic language. The resulting relationships between thermodynamic parameters (equilibrium constants, stoichiometric coefficients, etc.) and kinetic parameters (rate constants, reaction orders, etc.) will clearly have meaning only for those reactions for which the equilibrium state involves appreciable concentrations of both reactants and products, i.e., for "reversible" reactions, in the colloquial sense of this terminology (see section III.C.1).

It is possible to derive these relationships in a purely formal way, paying no heed to chemical mechanisms; such results are useful in a phenomenological sense, since they ensure that a rate law proposed for some new complex reaction is at least consistent with the thermodynamic description. However, chemists are not usually satisfied with a purely empirical description of a reaction rate, but demand some understanding of the mechanism underlying such a description of the overall rate. By starting with the usual assumption that any complex chemical reaction may be understood as a sequence of elementary chemical steps, it will be shown that certain relationships may be derived which resulted from purely formal considerations; however, starting from the idea of a chemical mechanism, this approach permits a much more complete understanding of these relationships, and in favorable cases permits conclusions to be drawn regarding the mechanism. The principle of detailed balance is crucial here; it seems not to be generally appreciated that, in a very large number of cases, this principle is a purely macroscopic requirement. The microscopic justification of this principle, when this is required, is the subject of section III.

A. Two-Term Rate Laws

1. Notation

First, it will be necessary to establish some general notation; consider the balanced stoichiometric equation for an overall chemical reaction involving stable species:

$$0 = \sum_{i=1}^l \nu_i(A_i) \quad (5)$$

involving the l chemical species A_i . The stoichiometric coefficients ν_i are positive for products, negative for reactants. Equation 5 is intended to represent *only* the overall stoichiometry of the reaction, with no mechanistic implications; the reaction is assumed to proceed spontaneously in a closed system at a constant temperature and volume. Then, at equilibrium:

$$K^*(T) = \prod_{i=1}^l (a_i^*)^{\nu_i} \quad (6)$$

where the superscript * denotes equilibrium conditions, a_i is the thermodynamic activity of A_i defined with reference to some specific standard state, and K^* is the thermodynamic equilibrium constant for the reaction described by eq 5. The thermodynamic affinity of the reaction described by eq 5 is defined as:

$$A = - \sum_{i=1}^l \nu_i \mu_i \quad (7)$$

where $\mu_i = \mu_i^0 + RT \ln a_i$. Then, at equilibrium, the affinity A

is zero; the reaction proceeds in the conventional left-to-right direction if $A > 0$, and in the reverse direction if $A < 0$.

The kinetic description, of the same reacting system, is not so clearcut. It must first be determined whether or not a unique reaction velocity may be defined; for a multistep reaction mechanism, this is far from a trivial requirement⁴⁻⁶ since different reactant species, for example, may transform via distinct reaction paths with different intrinsic rates. However, this is not often a serious problem, in practice. A more difficult question concerns the circumstances under which the chemical rate may be expressed as the difference of two terms;⁵ the importance of this question lies in the frequent identification of the two terms as being "forward and reverse rates", which balance at equilibrium. There is no specifically thermodynamic reason why the observed reaction must be expressible as the difference of two terms;² the frequent (though not invariable) occurrence of two terms in empirical rate equations must then be given a *kinetic* interpretation, and the conventional interpretation identifies the two terms with the forward and backward rates, these processes taking place simultaneously at the molecular level. While this interpretation is certainly consistent with a collisional mechanism, at least for elementary reactions, it is clear that the only observable is the net rate, and the concepts of "forward and backward rates" have meaning only by interpretation.² For reactions proceeding via several elementary reaction steps, the picture is even less clear in this regard.⁵

2. General Approach

For cases where it is found that a unique reaction velocity may be defined, and is given as the difference of two terms, it is possible⁷ to derive very general thermodynamic restrictions upon the rate equation, without specifying the details of the latter. Thus, suppose the unique velocity v of the reaction described by eq 5 is given by:

$$v = (1/\nu_i)(d(A_i)/dt) = u - u' \quad (8)$$

where u and u' are functions of the activities a_i , and possibly of other variables. It is mathematically convenient to further define:

$$f \equiv u'/u = f[a_1, a_2, \dots, a_l, x, y, \dots]$$

$$\Theta \equiv \prod_{i=1}^l [(a_i/a_i^*)^{\nu_i}]; \Theta^* = 1.0$$

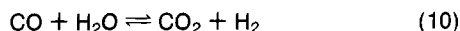
where x, y, \dots , etc., are nonthermodynamic variables such as catalyst concentration, area of catalytic surface, etc. It is now required to discover the conditions under which $f = 1$ if, and only if, $\Theta = 1$, i.e., under which the kinetic rate vanishes if, and only if, the thermodynamic criterion for equilibrium is fulfilled. Hollingsworth⁷ showed that, provided f has continuous derivatives of all orders, with respect to Θ , the necessary and sufficient conditions are: (a) $(f - 1)$ must be divisible by $(\Theta - 1)$, thus

$$(f - 1) = (\Theta - 1)\psi(a_1, a_2, \dots, a_l, x, y, \dots) \quad (9)$$

(b) the function ψ must have no zeros in the neighborhood of equilibrium ($\Theta = 1$).

This approach is generally valid and permits a consistency check to be made on any proposed two-term rate law like eq 8; in practice, the simplest method would seem to involve working through Hollingsworth's fairly brief procedure⁷ using the specific proposed rate functions, rather than attempting to apply the generalized result⁷ directly. This approach includes, as a special case, the earlier proposals due to Gadsby, Hinshelwood, and Sykes;⁸ the experimental data obtained by these workers⁸ for the water-gas reaction offer a good example of the applicability of Hollingsworth's method,⁷ and also a check upon it since the thermodynamic restrictions upon the rate equation were originally derived⁸ by a more intuitive, less systematic approach.

The water-gas reaction



occurs at high temperatures on a charcoal surface. The forward reaction was found⁸ to be first order in CO and of fractional order with respect to steam; it is retarded by both CO₂ and H₂, and the rate depended somewhat upon the nature of the charcoal catalyst. The forward rate expression u (eq 8) may thus be expressed by:

$$u = \frac{k_f(T)\phi_f(C)P_{\text{CO}}P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{1/m}f_1(P_{\text{H}_2}, P_{\text{CO}_2})} \quad (11)$$

where $m > 1$, $\phi_f(C)$ describes the effect of the catalyst C, and it has been assumed that all the temperature dependence may be included in k_f .

The reverse reaction rate was found⁸ to be of fractional order with respect to both H₂ and CO₂, retarded by steam, unaffected by CO, and to depend upon the catalyst:

$$u' = \frac{k_r(T)\phi_r(C)P_{\text{H}_2}P_{\text{CO}_2}}{P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}f_2(P_{\text{H}_2\text{O}})} \quad (12)$$

where $p > 1$, $q > 1$. Equations 11 and 12 are the simplest expressions consistent with the experimental findings;⁸ now, Hollingsworth's method⁷ will be applied to determine what further restrictions apply to u and u' as a result of the requirement that eq 8 vanish at thermodynamic equilibrium. Using Hollingsworth's notation⁷

$$f(P_{\text{CO}}, P_{\text{H}_2\text{O}}, P_{\text{H}_2}, P_{\text{CO}_2}, T, C) = \left(\frac{k_r}{k_f}\right) \left(\frac{\phi_r}{\phi_f}\right) \left[\frac{P_{\text{H}_2\text{O}}^{1/m}f_1(P_{\text{H}_2}, P_{\text{CO}_2})}{P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}f_2(P_{\text{H}_2\text{O}})}\right] \left(\frac{P_{\text{CO}_2}P_{\text{H}_2\text{O}}}{P_{\text{CO}}P_{\text{H}_2\text{O}}}\right) \quad (13)$$

i.e.

$$f^0(\Theta, P_{\text{H}_2\text{O}}, P_{\text{H}_2}, P_{\text{CO}_2}, T, C) = \left(\frac{k_r}{k_f}\right) \left(\frac{\phi_r}{\phi_f}\right) \left[\frac{P_{\text{H}_2\text{O}}^{1/m}f_1(P_{\text{H}_2}, P_{\text{CO}_2})}{P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}f_2(P_{\text{H}_2\text{O}})}\right] K\Theta \quad (14)$$

where $\Theta = (P_{\text{CO}_2}P_{\text{H}_2}/K P_{\text{H}_2\text{O}}P_{\text{CO}})$, and $K(T)$ is the equilibrium constant; thus, f^0 is the ratio of reverse to forward rates, but expressed using Θ to replace one of the reactant concentrations (P_{CO} in the present case). The reason for thus transforming f (eq 13) to f^0 (eq 14) is that $\Theta = 1$ at equilibrium; thus we require the conditions under which $f^0 \equiv 1$ at $\Theta = 1$, for all arbitrary sets of values of the remaining variables in eq 14. To discover these, f^0 is expanded⁷ about equilibrium ($\Theta = 1$), keeping the remaining variables fixed at some arbitrary set of values; in the present example, this expansion is a trivality, since $(\partial^n f^0 / \partial \Theta^n) = 0$, for $n > 1$. Thus, eq 14 becomes:

$$(f^0 - 1) = (\Theta - 1) \left\{ \left(\frac{k_r}{k_f}\right) \left(\frac{\phi_r}{\phi_f}\right) K \left[\frac{P_{\text{H}_2\text{O}}^{1/m}f_1(P_{\text{H}_2}, P_{\text{CO}_2})}{P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}f_2(P_{\text{H}_2\text{O}})}\right] \right\} \quad (15)$$

At equilibrium $\Theta = 1$, so eq 15 shows that $f^0 \equiv 1$ is guaranteed for any arbitrary set of the variables consistent with equilibrium, provided the expression in $\{ \}$ brackets has no zeroes near equilibrium. In order to elucidate the further implications of this consequence of the form of the chosen rate equation, it is best⁷ to replace eq 15, which involves Θ , by its counterpart involving P_{CO} ; thus, f^0 (eq 14) becomes the corresponding f (eq 13). Substitution of the appropriate expressions for $(f - 1)$ and $(\Theta - 1)$, and cancellation of terms leads, after some tedious algebra, to the following result:

$$k_f(T)\phi_f(C)P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}f_2(P_{\text{H}_2\text{O}}) = K(T)k_r(T)\phi_r(C)P_{\text{H}_2\text{O}}^{1/m}f_1(P_{\text{H}_2}, P_{\text{CO}_2}) \quad (16)$$

where the identity must hold for any arbitrary set of values for the variables ($P_{\text{H}_2\text{O}}, P_{\text{H}_2}, P_{\text{CO}_2}, T, C$). [Note: P_{CO} does not appear in this set, since this was the variable chosen to be replaced by Θ ; since eq 16 is an equilibrium condition, the value of P_{CO} is

fixed via $K(T)$ whenever an arbitrary set of the remaining variables has been chosen.] Clearly, eq 16 can be an identity, in the above sense, only if all the conditions collected in eq 17 are valid:

$$\begin{aligned} f_1(P_{\text{H}_2}, P_{\text{CO}_2}) &= P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q} \\ f_2(P_{\text{H}_2\text{O}}) &= P_{\text{H}_2\text{O}}^{1/m} \\ \phi_f(C) &= \phi_r(C) = \phi(C) \\ k_f(T)/k_r(T) &= K(T) \end{aligned} \quad (17)$$

Thus, the forward and reverse contributions to the net rate now become:

$$u = \left\{ \frac{k_f(T)\phi(C)P_{\text{CO}}P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{1/m}P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}} \right\}; u' = \left\{ \frac{k_f(T)\phi(C)P_{\text{H}_2}P_{\text{CO}_2}}{K(T)P_{\text{H}_2\text{O}}^{1/m}P_{\text{H}_2}^{1/p}P_{\text{CO}_2}^{1/q}} \right\} \quad (18)$$

where the rate expression is now guaranteed to vanish at equilibrium, as required. There remains the question as to whether this rate expression can vanish under any conditions other than those of equilibrium; this is *not* possible in the present case, as can be readily seen from eq 15, which now, using eq 17, reduces to:

$$(f^0 - 1) = (\Theta - 1) \times 1$$

Thus, $f^0 = 1$ (rate expression vanishes) if, and only if, $\Theta = 1$ (thermodynamic equilibrium).

Essentially identical conclusions to those summarized in eq 18 were derived, by a much more direct approach, by Gadsby, Hinshelwood, and Sykes.⁸ However, the advantage of Hollingsworth's procedure⁷ is that it is general and systematic, and may thus be usefully applied in more complicated cases.

3. Simple Kinetic Order Rate Laws

The very general method due to Hollingsworth⁷ can be tedious and cumbersome to apply. The consistency of kinetic and thermodynamic prescriptions for equilibrium can be guaranteed by a much simpler procedure, in the case that the rate equation takes the following form:

$$v = (1/v_i)[d(A_i)/dt] = k\beta \prod_{i=1}^m (a_i)^{\omega_i} - k'\beta' \prod_{i=1}^m (a_i)^{\omega_i'} \quad (19)$$

The rate constants k and k' are functions of temperature only, provided that provision is made for the dependence upon such variables as total ionic strength via the factors β and β' ; empirically, it turns out² to be perfectly satisfactory to set $\beta' = \beta$. This is understandable for elementary reactions, to which transition state theory is applicable, since β may be interpreted² as the reciprocal of the activity coefficient of the activated complex. The integer m enumerates all species whose activities affect the rate directly, i.e., other than via β ; it is thus possible that $m > 1$, since catalytic species do not appear in the stoichiometric eq 5. The numbers ω_i and ω_i' are the empirically determined reaction orders, not necessarily equal to the stoichiometric coefficients ν_i ; for catalytic species, it will become apparent that $\omega_i = \omega_i'$.

The first investigation of thermodynamic restrictions upon rate laws like eq 10 appears to be due to Denbigh and Prince,⁹ who applied their principle in elucidating the kinetics for the heterogeneous reaction: $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$. Further elucidation of the principles involved has since appeared in the literature;¹⁰⁻¹³ the following discussion is based upon the most recent treatment,¹³ suitably generalized to take proper account of catalytic species, ($\nu_i = 0$ in eq 5).

It will now be shown that eq 20 is the necessary and sufficient condition under which the rate (eq 19) vanishes when the thermodynamic equilibrium condition (eq 6) is satisfied:

$$\begin{aligned} k/k' &= K^\phi, \text{ where } \phi = (\omega_i' - \omega_i)/\nu_i, \text{ for all } 1 < i < l \\ \omega_i' &= \omega_i, \text{ for } \nu_i = 0 \end{aligned} \quad (20)$$

In order to prove that eq 20 is indeed a necessary condition, it must be shown that, if some arbitrary set of equilibrium activities $\{a_i^*\}$ may be assumed to simultaneously satisfy eq 6 and set the velocity (eq 19) to zero, then eq 20 is a logical consequence of this assumption. Thus, it is first assumed that a set $\{a_i^*\}$, satisfying eq 6, corresponds to a zero value for v , so that:

$$k/k' = \prod_{i=1}^m [(a_i^*)^{(\omega_i' - \omega_i)}] \quad (21)$$

The factors β and β' have here been set equal to one another as discussed above. Since each of k , k' , and K^* is a function of temperature *only*, it must be true that K^* is a function of (k/k') :

$$K^* = g(k/k') \quad (22)$$

(The definitions of K^* , k , and k' used here are such that both K^* and (k/k') are dimensionless.) If now eq 6 and eq 21 are substituted into eq 22, we obtain:

$$\prod_{i=1}^l (a_i^*)^{v_i} \equiv g \left[\prod_{i=1}^m (a_i^*)^{(\omega_i' - \omega_i)} \right] \quad (23)$$

where eq 23 is an identity in the sense that it must hold for all equilibrium sets of activities $\{a_i^*\}$. Then, choose all $a_i^* = 1.0$, except for some a_j^* , where $1 \leq j \leq l$ (i.e., for any species with $v_j \neq 0$, which is involved in the overall stoichiometry). Then, eq 23 becomes

$$(a_j^*)^{v_j} = g[(a_j^*)^{(\omega_j' - \omega_j)}] \quad (24)$$

For convenience, set $a_j^* = z^{1/(\omega_j' - \omega_j)}$, so that eq 24 becomes:

$$g(z) = z^{v_j/(\omega_j' - \omega_j)} = z^{1/\phi}, \text{ where } \phi = (\omega_j' - \omega_j)/v_j \quad (25)$$

Now, a_j^* was chosen completely arbitrarily, so that eq 25 holds for all j such that $1 \leq j \leq l$ (i.e., $v_j \neq 0$); also, from the definition of a function, eq 22 and eq 25 give:

$$K^* = g(k/k') = (k/k')^{1/\phi} \quad (26)$$

Equation 26 is that part of eq 20 applicable for $v_j \neq 0$; for $l < j \leq m$ (i.e., for catalytic species, for which $v_j = 0$), eq 24 becomes:

$$1 = g[(a_j^*)^{(\omega_j' - \omega_j)}] \quad (27)$$

Since the value of a_j^* is quite arbitrary for a catalytic species, eq 27 requires:

$$g[(a_j^*)^{(\omega_j' - \omega_j)}] = (a_j^*)^0, \text{ or } \omega_j' = \omega_j \quad (28)$$

This is the second half of eq 20, which has now been shown to be a necessary condition; proof of the sufficiency of this condition requires a demonstration that, if eq 20 is assumed to hold, then any set of equilibrium activities satisfying eq 6 also satisfies the *kinetic* equilibrium condition eq 21, and vice versa. This proof is a simple exercise in algebraic substitution. Thus, eq 20 is the necessary and sufficient condition under which thermodynamic and kinetic criteria of equilibrium are identical, for rate equations like eq 19. It is also readily proved¹³ that $\phi > 0$ if product species ($v_j > 0$) are defined as those species whose concentrations increase as the affinity (eq 7) decreases.

The elementary derivation of the rate quotient law (eq 4) given in section I has now been replaced by the above treatment; the general result (eq 20) becomes the rate quotient law if $\phi = 1$. The kinetic orders of reaction (ω_i and ω_i' in eq 19) are empirical constants; however, there is a degree of arbitrariness in the stoichiometric coefficients v_i . By a simple redefinition of these numbers by multiplying through the stoichiometric equation (eq 5) by ϕ , K^* becomes $K' \equiv (K^*)^\phi$, and eq 20 reduces to the rate quotient law.

This reduction clearly depends upon the significance to be attached to the stoichiometric coefficients, whose ratios are unambiguously defined; there is, however, no accepted convention for normalizing them. In thermodynamics, the importance of stoichiometry lies in the implied relationships between the masses of the various substances involved in the chemical reaction, and eq 5 is probably best rewritten, for such purposes, in the form:

$$0 = \sum_{i=1}^l v_i M_i \quad (29)$$

where M_i is the molecular weight of species A_i . In such a purely macroscopic context, the magnitudes (though not the ratios) of the v_i are clearly completely arbitrary. However, this is not so if the stoichiometric equation is also to be interpreted in any additional sense related to molecular mechanism; in particular, fractional values of the stoichiometric coefficients would then be meaningless. Thus, the suggested reduction of eq 20 to the rate quotient law is of no concern to thermodynamics, but might conflict with mechanistic interpretations of the reaction. Further discussion of this question will be deferred until the mechanistic implications of the parameter ϕ (eq 20) have been examined. However, it is clear that eq 20 *does* reduce to the rate quotient law at least for elementary reactions, for which $\phi = 1$ since:

$$\begin{aligned} \omega_i &= -v_i, \omega_i' = 0, \text{ for } v_i < 0 \text{ (reactants)} \\ \omega_i &= 0, \omega_i' = v_i, \text{ for } v_i > 0 \text{ (products)} \\ \omega_i &= \omega_i', \text{ for } v_i = 0 \text{ (catalysts)} \end{aligned} \quad (30)$$

For the water-gas reaction, discussed above in terms of Hollingsworth's general approach,⁷ it turns out (eq 18) that the rate equation is of the form of eq 19, with $\phi = 1$. This latter result was implicitly assumed by Gadsby, Hinshelwood, and Sykes⁸ as being a necessary condition; as pointed out later,¹⁰ however, this is unnecessarily restrictive. That $\phi = 1$, in fact, for the water-gas reaction is an experimental⁸ finding (e.g., $\omega'_{CO} = 0$, $\omega_{CO} = 1$, $v_{CO} = -1$), *not* a theoretical requirement.

The treatment, thus far, has been essentially a simple exercise in pure mathematics, in the sense that the results are consequences solely of the structure of the relevant equations. No account has been taken of the physical interpretation of the quantities appearing in these equations; thus, for example, no physical meaning attaches to the parameter ϕ in eq 20, at present. This may be achieved by an alternative approach, described below.

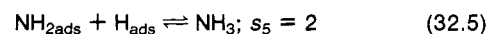
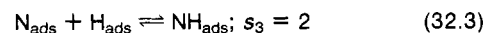
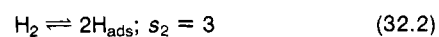
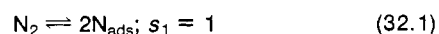
4. Chemical Mechanism Approach

The approach to be described below is due to the work of Horiuti and his collaborators,^{6,15-18} applications to electrochemical kinetics have been reviewed by Conway,¹⁹ and Horiuti himself has given a general review¹⁸ of the results obtained.

This treatment starts from the purely chemical notion that any overall chemical reaction, described by eq 5, may in principle be decomposed into a set of elementary reaction steps; thus using an example proposed by Horiuti, the catalyzed synthesis of ammonia is described by the overall stoichiometric relation:



A feasible sequence of elementary steps for this reaction is given¹⁸ as



The subscript ads denote the adsorbed state of the species on the catalyst; all other species are understood to be in the gas phase. The s_i are the stoichiometric numbers¹⁸ of the corresponding elementary steps, eq 32. i ; these should not be confused with the stoichiometric coefficients of reaction species, introduced in eq 5. The stoichiometric numbers are such that the overall reaction eq 31, with zero net creation or destruction of intermediates, is given by a linear combination of the elementary steps eq 32. i , where the coefficients in the linear combination are given by the appropriate s_i .

A general relation, between the kinetic parameters and the equilibrium constant, for the overall reaction may now be readily derived by using the principle of detailed balance. This principle is discussed in some detail below, but for present purposes it will suffice to state and use the principle, leaving the justification till later. For a multistep reaction mechanism like eq 32, detailed balance requires that when the complete system is at equilibrium, each individual elementary step must be at equilibrium, e.g., for the elementary chemical reaction 32.1 at complete equilibrium:

$$\text{rate of elementary step 32.1 at equilibrium} = 0 \\ = k_1\beta_1 a^*_{N_2} - k_1'\beta_1'(a^*_{N(\text{ads})})^2 \quad (33)$$

It is the first line of eq 33 which represents the principle of detailed balance, as stated above; the second line of eq 33 represents a basic assumption of chemical kinetics, viz. that the rate equations for elementary reactions are simple forms of eq 19, with the reaction orders given directly by the stoichiometric coefficients via eq 30. It is, of course, frequently possible to check this assumption experimentally; in other cases, the assumption is justified by an appeal to the concept of molecular collisions as a necessary prerequisite for an elementary reaction. Molecular encounter rates, whether in the gaseous or condensed phases, are known to be proportional to the concentrations of the colliding species. In any event, when reference is made to the *chemical* principle of detailed balance, it is usually *both* lines of eq 33 which are implicitly invoked; then, this principle is frequently rewritten (setting $\beta = \beta'$), as $(k_1/k_1') = (a^*_{N(\text{ads})})^2/a^*_{N_2} = K_1^*$, and similarly for each of the other elementary steps. Since the s_i were defined so that the corresponding linear combination yields zero net production of intermediates, it follows that, on using detailed relations like eq 33:

$$(k_1/k_1')^1(k_2/k_2')^3(k_3/k_3')^2(k_4k_4')^2(k_5k_5')^2 \\ = (a^*_{NH_3})^2/(a^*_{N_2})(a^*_{H_2})^3 = K^* \quad (34)$$

i.e., activities of intermediates cancel in the continued product. It is clear that eq 34 may be generalized¹⁸ to:

$$\prod_{\gamma=1}^S (k_\gamma/k_\gamma')^{s_\gamma} = K^* \quad (35)$$

where K^* is the equilibrium constant for the overall reaction (eq 5), assumed to proceed via a single sequence of S elementary steps. (Additional problems associated with several parallel sequences are discussed below.) It is clear that the question as to whether eq 35 can be reduced to eq 20 is bound up with the question as to whether the multistep mechanism described by eq 32 can yield a rate law like eq 19; the present treatment follows two previous treatments^{5,18} in deriving a sufficient condition under which this question yields a positive answer.

Since all the mechanistic steps are, by definition, elementary reactions, then for each step α , $\omega_i^\alpha = -v_i^\alpha$ for any species i appearing as a reactant in step α , and $\omega_j^{\alpha'} = v_j^\alpha$ for any species j appearing as a product in step α . Then, the rate of reaction α may be written as $v_\alpha = u_\alpha - u_\alpha'$, where:

$$u_\alpha/u_\alpha' = (k_\alpha/k_\alpha')/Q_\alpha(a_i) \quad (36)$$

where $Q_\alpha(a_i)$ is the activity quotient⁵ for reaction step α ; i.e., the same function of the nonequilibrium activities as K_α^* is of

the equilibrium activities appropriate to step α . Then, again as a consequence of the definition of the s_α , the activities of intermediate species cancel in the following product:

$$\prod_{\gamma=1}^S (u_\gamma/u_\gamma')^{s_\gamma} = \prod_{\gamma=1}^S (k_\gamma/k_\gamma')^{s_\gamma}/Q(a) \quad (37)$$

where $Q(a)$ is the activity quotient of the overall reaction, i.e., the nonequilibrium analogue of K^* . Combining eq 35 and eq 37 gives:

$$\prod_{\gamma=1}^S (u_\gamma/u_\gamma')^{s_\gamma} = K^*/Q(a) \quad (38)$$

It is now supposed that the reaction mechanism in question is such that the elementary steps are all at equilibrium except for the single step $\gamma = \alpha$; this has been referred to^{5,18} as a rate-determining step, and the meaning of this term is at least unambiguous in the present context. However, indiscriminate use of this term may lead to confusion,²⁰ and in using this term here no implications are intended other than those described above. Then, under this assumption, it is clear that eq 38 becomes:

$$u_\alpha/u_\alpha' = [K^*/Q(a)]^{1/s_\alpha} \quad (39)$$

Further, under the above equilibrium assumption, it is clear that the overall rate of reaction $v = v_\alpha/s_\alpha$, and also that the "forward" and "reverse" rates for the overall reaction are:

$$u = u_\alpha/s_\alpha \text{ and } u' = u_\alpha'/s_\alpha \quad (40)$$

then combining eq 39 and eq 40 yields:

$$u/u' = [K^*/Q(a)]^{1/s_\alpha} \quad (41)$$

(While each of u_α and u_α' are simple expressions, involving the activities of at least some intermediate species, u and u' , on the other hand, involve only the activities of stable molecules appearing in eq 5; u_α and u_α' may be related to u and u' through the equilibrium assumption^{5,18} which was made above.) A direct comparison of eq 41 with eq 20 gives:

$$u/u' = (k/k') \prod_{i=1}^m (a_i^{\omega_i - \omega_i'}) \\ = (K^*)^\phi \prod_{i=1}^l (a_i^{\phi v_i}) = [K^*/Q(a)]^\phi \quad (42)$$

Comparing eq 41 and eq 42 gives the identification $\phi \equiv 1/s_\alpha$; thus, the approach of Horiuti¹⁸ permits clarification of the circumstances under which a simple rate equation like eq 19 can arise from a complex mechanism, and also allows a physical meaning to be placed upon the parameter ϕ of eq 20. This condition, viz. just one elementary mechanistic step in disequilibrium, is clearly sufficient but is possibly not necessary. Thus, conventional steady-state treatments of complex mechanistic schemes *can* yield simple mass-action rate laws like eq 19, although *usually* the rate laws predicted in this way are more complicated, and reduce to the form of the latter in some appropriate "equilibrium" limit.

As an example of the utility of the Horiuti approach,¹⁸ as compared with the purely empirical treatment given in section II.A.3, the reaction system studied by Denbigh and Prince⁹ will be reexamined. This will also provide a concrete example for further discussion of the additional attributes of stoichiometric coefficients when chemical equations are understood to carry mechanistic implications.

The overall stoichiometry of the reaction is:



Equation 43 has been written in terms of N_2O_4 rather than NO_2 , since the former was the dominant species at the temperatures used;⁹ also, experimental evidence was obtained⁹ to

suggest that N_2O_4 was indeed the active substance. In addition, eq 43 has been written with no fractional coefficients, and the significance of this choice will become apparent later.

The discussion will be considerably simplified if restricted to conditions of constant temperature and constant concentration of nitric acid; this implies that both P_{H_2O} and P_{HNO_3} are constant, so that the equilibrium condition becomes:

$$(P_{NO}^2/P_{N_2O_4})_{eq} = K' = K_P(P_{H_2O}^2/P_{HNO_3}^2) \quad (44)$$

where $K_P = (P_{NO}^2 P_{HNO_3}^2 / P_{N_2O_4}^2 P_{H_2O}^2)_{eq}$ is the true equilibrium constant, assuming the vapors to be ideal gases. The rate of the forward reaction, normalized to unit area of vapor-liquid interface, was found⁹ to be:

$$u = kP_{N_2O_4} \quad (45)$$

The reverse reaction rate was shown⁹ to depend on the partial pressures of both N_2O_4 and NO and was written as:

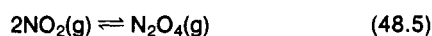
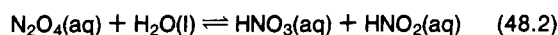
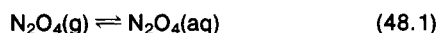
$$u' = k' P_{N_2O_4}^p P_{NO}^q \quad (46)$$

with the net normalized rate $v = (u - u')$, for fixed temperature and nitric acid composition. Application of the purely formal result eq 20 imposes the following restriction⁹ upon p and q :

$$(p - 1)/(-3) = \phi = (q/2) \quad (47)$$

This establishes the requirement $(1 - p) = 3q/2$, but does not in itself specify unique values for p and for q . By trial and error, it was determined⁹ that the pair of values ($p = 1/4$, $q = 1/2$) accounted well for the kinetic data, thus implying $\phi = 1/4$ in this case.

Denbigh and Prince⁹ also discussed the probable mechanism of the reaction and were able to reconcile their experimental value $\phi = 1/4$ with this mechanism by working through the rate equations in detail; this reconciliation will now be effected using the general result (eq 41) of Horiuti.¹⁸ The proposed sequence of elementary steps may be written as follows:



(The notation (aq) is taken⁹ to denote the surface layer of the aqueous phase, thus accounting for the observed dependence of the rate on the interfacial area.)

The fashion in which these *elementary* reaction steps have been written assumes critical importance at this point. In accord with their mechanistic implications, the stoichiometric coefficients in each step must be integers; in the same way, due to the low probability of molecular encounters more complex than bimolecular (or possibly termolecular if one of the molecules involved is solvent, e.g., reverse of eq 48.3), these integers must be small enough that their sum, for either reactants or products of a specific step, must be no greater than two (or possibly three, occasionally). This restriction is clearly totally foreign to thermodynamics, and amounts to much the same thing as the familiar idea that, for an elementary reaction, the kinetic order is the same as the molecularity (see discussion following eq 33, above, and eq 30).

If the mechanism (eq 48) is to account for the observed net reaction (eq 43), with zero net formation or destruction of intermediates, the set of stoichiometric numbers¹⁸ must be:

$$\{s_1 = 4; s_2 = 4; s_3 = 2; s_4 = 2; s_5 = 1; s_6 = 2\} \quad (49)$$

All stoichiometric numbers must be integers, if the molecular

implications of the mechanism (eq 48) are to be retained; thus, the set $\{s_i\}$ given as eq 49 represents the minimum values for the postulated mechanism, since $s_5 = 1$. Therefore the overall reaction may not be described by a stoichiometric equation derived from eq 43 by dividing through by a number greater than unity, if the mechanistic interpretation is to be taken seriously. Further, if each step in eq 48 is to be taken as representing an elementary process at the *molecular* level (and this is surely the entire point of such mechanistic proposals), the set $\{s_i\}$ given by eq 49 also represents the maximum values, and the overall stoichiometry expressed by eq 43 is correspondingly unique. Thus, in pure thermodynamics the stoichiometric coefficients are entirely arbitrary provided only that their ratios are maintained, and thus so is ϕ (eq 20) arbitrary; on the other hand, if the same overall reaction is considered in terms of molecular mechanisms, the arbitrariness of the stoichiometric coefficients arises only from that of the mechanism, with a unique set $\{v_i\}$ corresponding to any given mechanism, and a unique ϕ (eq 20).

Denbigh and Prince⁹ proposed that, under their reaction conditions, step 2 was rate determining in the sense defined above; i.e., all other steps are essentially at equilibrium. Then, according to Horiuti's result,¹⁸ $\phi = 1/s_2 = 1/4$, as was, in fact, experimentally determined. The only other possibility is that step 1 is rate determining; however, the behavior of the rate upon varying the HNO_3 concentration indicated that step 2 was the correct choice.

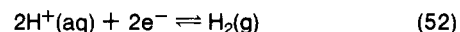
An assumption implicit in the treatment so far is the existence of a single, unique reaction with for the overall reaction, i.e., of a unique linear combination $\{s_i\}$ corresponding to the overall stoichiometry. It was elegantly demonstrated by Horiuti and Nakamura¹⁶ that, for a mechanism comprised of S elementary reaction steps involving I independent¹⁶ intermediates, the number P of independent reaction routes (i.e., of linearly independent sets of stoichiometric number $\{s_i\}$), is given by:

$$P = S - I \quad (50)$$

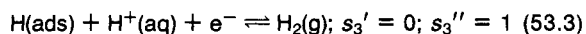
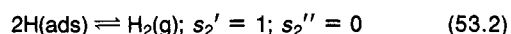
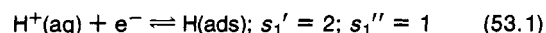
The meaning and method of computation of I will be described below. Both in derivation and in meaning, eq 50 is very similar to Gibbs' phase rule; the number of elementary reaction steps S is analogous to the number of coexisting phases, the number of independent intermediates I corresponds to the number of components, and P is the number of degrees of freedom. In this more general case, Horiuti¹⁷ has shown that the relationship between the kinetic and thermodynamic parameters may be expressed as:

$$\prod_{\gamma=1}^S (k_{\gamma}/k_{\gamma}')^{s_{\gamma}(q)} = K^*, \text{ for } 1 \leq q \leq P \quad (51)$$

where $s_{\gamma}(q)$ is the stoichiometric number of the γ th elementary reaction step as it appears in the q th reaction route. Again, the question as to whether a multiroute mechanism ($P > 1$) can give rise to a relationship like eq 20 is bound up with the question as to the existence of a simple rate law like eq 19. For this to be true, it would seem to be necessary that all P routes have a common rate-determining step, in the limited sense of this term as used above. Some problems inherent in this supposition may be illustrated¹⁸ by reference to the electrolytic hydrogen-evolution reaction:



A set of postulated elementary steps which yield this overall reaction, via more than one route, is:



Here, $S = 3$, $I = 1$ (the only intermediate is $H(\text{ads})$), so $P = 2$; there are thus just two linearly independent sets $\{s_i\}$ which yield eq 52 as a linear combination of eq 53.1. The two sets $\{s_i'\}$ and $\{s_i''\}$, given above, are one possible choice.

Suppose that it is postulated that the reaction actually proceeds via the two routes $\{s_i'\}$ and $\{s_i''\}$, simultaneously; further suppose that the common step eq 53.1 is rate determining in both routes, thus permitting a simple rate law like eq 19. However, this apparently reasonable supposition in fact contains a self-contradiction,¹⁸ for if true, the most rapid route for the reaction would not involve eq 53.1 at all, but only the two rapid steps, eq 53.2 and eq 53.3, i.e., the route $\{s_1''' = 0, s_2''' = -1, s_3''' = +2\}$.

Thus, as first suggested by Horiuti,¹⁸ it seems unlikely that a simple rate law like eq 19 could ever arise from a multiroute mechanism. This is because, given two or more linearly independent reaction routes with a common postulated rate-determining step, it is always possible to devise a linear combination of these routes such that the stoichiometric number of the proposed rate-determining step is zero. Thus, the preferred (fastest) route will *not* involve the postulated rate-determining step, which is thus excluded from consideration. It may be thought possible that all other stoichiometric coefficients in the new route may possibly be also zero; this possibility, however, is excluded because the original routes considered, $\{s_i'\}$ and $\{s_i''\}$, were linearly independent.

It now remains, in this section, to clarify the meaning of the parameter I , the number of "independent" intermediates (eq 50). The restrictions upon any acceptable set $\{S_\gamma\}$, i.e., upon an acceptable reaction path based upon the proposed mechanistic steps, are that the correct net stoichiometry for the overall reaction must result, with zero net creation or destruction of postulated intermediates. If there are J of the latter, then the constraint based upon the intermediates may be written:

$$\sum_{\gamma=1}^S v_{j\gamma} S_\gamma = 0, \text{ for } 1 \leq j \leq J$$

where $v_{j\gamma}$ is the stoichiometric coefficient of intermediate j in step γ ; this may be conveniently expressed in matrix form:

$$\mathcal{V}_{JS} |S\rangle_S = |0\rangle_J \quad (54)$$

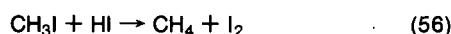
where \mathcal{V}_{JS} is the $J \times S$ matrix of the stoichiometric coefficients $v_{j\gamma}$, $|S\rangle_S$ is a $S \times 1$ column vector whose γ th component is S_γ , and $|0\rangle_J$ is a $J \times 1$ null vector. In general, $J \neq S$ (usually $J < S$). What is required is P , the number of linearly independent solutions $\{S_\gamma\}$ to the system of homogeneous linear equations, eq 54. As is shown in almost any text on linear algebra, the critical quantity is the rank I of the matrix \mathcal{V}_{JS} , i.e., the order of the largest nonzero minor of the matrix. Then, since there are S unknowns (the S_γ), it is a standard theorem of linear algebra that the number P of linearly independent solutions $\{S_\gamma\}$ is given by eq 50. Thus, the mathematical definition of I is that it is the rank of the stoichiometric coefficient matrix of intermediates \mathcal{V}_{JS} ; the further physical interpretation of I is given below.

Before doing so, however, it should be noted that sets $\{S_\gamma\}$ consistent with eq 54 (zero net production of each and every intermediate) are not necessarily acceptable; a further condition is that $\{S_\gamma\}$ shall lead to the correct overall stoichiometry:

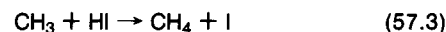
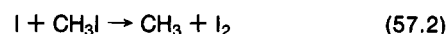
$$\prod_{\gamma=1}^S v_{i\gamma} S_\gamma = v_i, \text{ for } 1 \leq i \leq I \quad (55)$$

where i labels reactants and products appearing in the net reaction (eq 5). Thus, an acceptable set $\{S_\gamma\}$ must also satisfy eq 55.

The physical interpretation of I is best illustrated by an example. The thermal decomposition of CH_3I in a large excess of HI proceeds according to the overall stoichiometry:



and an acceptable mechanism might be:



There are two intermediates, I and CH_3 , and four proposed mechanistic steps, so the matrix \mathcal{V}_{JS} becomes:

$$\mathcal{V}_{24} = \begin{pmatrix} 2 & -1 & 1 & -2 \\ 0 & 1 & -1 & 0 \end{pmatrix} \quad (58)$$

The rank of this matrix is clearly 2, so there are two independent routes based upon eq 57, e.g., $\{S_\gamma\} = \{1, 1, 1, 1\}$ and $\{S_\gamma\} = \{0, 1, 1, 0\}$, both of which are consistent with eq 56. Thus, in this case the two intermediates (CH_3 and I) are regarded as independent.

On the other hand, if a mechanism were proposed comprising *only* eq 57.2 and eq 57.3, the rank of the corresponding \mathcal{V}_{22} is clearly one, so there is just one permissible reaction path, and just one *independent* intermediate. The difference between the two proposed mechanisms is that, in the first, I atoms are produced and destroyed by at least one step not involving CH_3 , whereas in the second, shorter mechanism, every step destroying an I atom creates a CH_3 , and vice versa. Thus, these are not, in this case, "independent" intermediates in the sense of Horiuti.¹⁶ Mathematically, the latter situation corresponds to rows in the matrix \mathcal{V}_{JS} which are not linearly independent.

Finally, in this section, it should be emphasized that the present considerations are limited to reaction mechanisms in which all elementary reactions are kinetically "reversible" (see section III.C, below), under the conditions of the experiment; it is only for such systems that comparison of kinetic and thermodynamic criteria for equilibrium is meaningful for a given reaction mixture; i.e., the equilibrium constant is not extremely large or extremely small. For cases in which the overall reaction, and thus at least some of the elementary steps, is irreversible (i.e., the overall equilibrium constant is extremely large, or else a "trapping" experiment is being considered), the treatment requires an understanding of microscopic reversibility and detailed balance, which are discussed below.

5. Rate Coefficients

A crucial restriction in the discussion thus far was the stipulation that k and k' are functions of temperature *only*; this corresponds to experimental observation, and rate constants obtained from experiments using a given reaction mixture composition may be successfully used to predict rates in reaction mixtures of *any* composition, at the same temperature (portability property). The term "rate constant" will, for present purposes, be restricted to parameters appearing in rate equations like eq 19, and which fulfill the portability condition. Thus, as shown above, the validity of relations like eq 20 depends only on the validity of eq 19, where k and k' are rate constants in this restricted sense. Parameters derived as the ratio of an observed rate to a simple function of activities, without demonstration of their independence of time and of composition, will be referred to as "rate coefficients".

The question of the applicability of the rate quotient law, i.e., of eq 20 with $\phi = 1$, to such rate coefficients has been considered²¹ for the special case of an isomerization reaction $\text{R} \rightleftharpoons \text{P}$, in a thermodynamically ideal system. The following rate equation might then be *assumed* (i.e., without experimental verification):

$$-d(\text{R})/dt = C(\text{R}) - C'(\text{P}) \quad (59)$$

where C and C' are rate coefficients, possibly functions of time

and of chemical composition. By using the mass-conservation condition $(R) + (P) = (T) = (R^*) + (P^*)$, and defining $(C/C') \equiv K^*$, the following operational definitions of C and C' are consistent with eq 59:

$$C = -(1 + K^{*-1})^{-1}(d/dt)[\ln\{(R) - (T)(1 + K^*)^{-1}\}]$$

$$C' = -(1 + K^*)^{-1}(d/dt)[\ln\{(P) - (T)(1 + K^{*-1})^{-1}\}] \quad (60)$$

In this sense,²¹ even rate coefficients obey eq 20; however, the significance of this result is not clear. In the definitions, eq 60, K^* could be replaced by any dimensionless number whatsoever, thus defining rate coefficients which are perfectly consistent with eq 59, but whose ratio is completely arbitrary. The point is simply that the most striking feature of chemical kinetics is not eq 20 per se, but rather the fact that rate equations like eq 19 give such a generally satisfactory description of rates of chemical change², where k and k' are functions of temperature only. The rate could be expressed in terms of any functional form whatsoever, provided one is content to use parameters which depend on time and/or composition. For example, the phenomenological coefficients of nonequilibrium thermodynamics are, for the case of chemical reaction, functions of the equilibrium composition of the system; this constitutes a considerable disadvantage of this description, as opposed to the conventional kinetic terminology.²²

B. Detailed Balance as a Macroscopic Requirement

The meaning of detailed balance, in the sense required by chemical kinetics, was explained with reference to a particular example in eq 33. In the present section, it will be shown that in many cases detailed balance is a purely macroscopic result;^{23,24} the following treatment, which closely follows that due to Gray,²³ derives the detailed balance condition, under certain restrictions, as a direct consequence of conservation of mass in a closed system at constant volume.

Using notation previously established, the total rate of change of species A_j may be written as:

$$\dot{A}_j \equiv d(A_j)/dt = \sum_{\gamma=1}^S v_{j\gamma} \{k_{\gamma} \beta_{\gamma} \prod_{i=1}^n (a_i \omega'_{i\gamma}) - k'_{\gamma} \beta'_{\gamma} \prod_{i=1}^n (a_i \omega_{i\gamma})\}$$

$$= \sum_{\gamma=1}^S v_{j\gamma} \{u_{\gamma} - u'_{\gamma}\} = \sum_{\gamma=1}^S v_{j\gamma} v_{\gamma} \quad (61)$$

where n is now the total number of chemical species (including intermediates) involved in the S elementary steps comprising the mechanism; $v_{j\gamma}$ is the stoichiometric coefficient of species j in elementary reaction γ , so that eq 30 applies for each γ , i.e., $\omega_{j\gamma} = -v_{j\gamma}$, for $v_{j\gamma} < 0$, and $\omega'_{j\gamma} = v_{j\gamma}$, for $v_{j\gamma} > 0$. (A_j) is the molar concentration of species A_j .

It is worth emphasizing here that in eq 61, and the ensuing treatment, all elementary reactions proposed for the mechanistic sequence are to be explicitly taken into account in deriving an expression for the net rate of production of each and every species involved in the mechanism. There is no question here of choosing a linearly independent set of mechanistic steps, as must be done for a treatment in terms of nonequilibrium thermodynamics, for example;^{3,78,79,81} procedures for determining the number of linearly independent reactions are well established.¹²⁴⁻¹²⁶ Reactions which are redundant in a thermodynamic sense are not redundant in kinetics; this is why they are included in the proposed mechanism. The importance of this point lies in the famous derivation of the chemical principle of detailed balance (eq 33) by Onsager,³ using an approach since developed into the field of nonequilibrium thermodynamics; this latter approach derives eq 33 (as a special form of the Onsager reciprocity theorem³), by considering the "thermodynamic coupling" between a linearly independent set of reactions. This coupling is simply an expression of the existence of thermodynamically

redundant, but mechanistically significant, reaction steps; this approach will not be emphasized here, as it offers a much less detailed description of a reaction system than is normally of interest to chemists. There are also serious disadvantages, in a purely practical sense, to the use of nonequilibrium thermodynamics in chemical kinetics.²²

Then, for a closed reaction system at constant volume, to which the rate equations (eq 61) apply, the total mass is conserved, and this may be expressed by:

$$\sum_{i=1}^n M_i \dot{A}_i = 0 \quad (62)$$

where M_i is the molecular mass of species i . Substitution from eq 61 for \dot{A}_i gives:

$$\sum_{i=1}^n M_i \sum_{\gamma=1}^S v_{i\gamma} v_{\gamma} = \sum_{\gamma=1}^S \left[\left(\sum_{i=1}^n M_i v_{i\gamma} \right) v_{\gamma} \right] = 0 \quad (63)$$

Now, the validity of the principle of conservation of mass does not depend upon all or some of the v_{γ} having zero values, but is valid for all conceivable values of the v_{γ} ; thus, the coefficient of each v_{γ} in eq 63 must separately be zero, i.e.

$$\sum_{i=1}^n v_{i\gamma} M_i = 0, \text{ for } 1 < \gamma < S \quad (64)$$

For comparison with eq 64, the rate expressions given by eq 61 will be written for the particular case of the equilibrium state:

$$\dot{A}_i^* = \sum_{\gamma=1}^S v_{i\gamma} v_{\gamma}^* = 0, \text{ for } 1 < i < n \quad (65)$$

It is clear that eq 64 and eq 65 may be written in matrix form, as eq 66 and eq 67, respectively:

$$(\mathcal{V}_{nS})^T |M\rangle_n = |0\rangle_n \quad (66)$$

$$\mathcal{V}_{nS} |v^*\rangle_S = |0\rangle_S \quad (67)$$

where $(\mathcal{V}_{nS})^T$ is the transpose of the matrix of stoichiometric coefficients \mathcal{V}_{nS} , for each and every species in each and every elementary reaction; the n th element of the n vector $|M\rangle_n$ is M_i , while the γ th element of the S vector $|v^*\rangle_S$ is v_{γ}^* . Each of eq 66 and eq 67 is a set of homogeneous linear equations, in the M_i and v_{γ}^* , respectively; the conditions, under which such sets of equations yield solutions other than the mathematically "trivial" null solution, e.g., $|v^*\rangle_S = |0\rangle_S$ for eq 67, again involve the rank of the matrix of coefficients. The present aim is to discover the conditions under which $|v^*\rangle_S = |0\rangle_S$ is the only solution, since such a circumstance corresponds to the first line of eq 33, the chemical principle of detailed balance. For a set of n linear homogeneous equations like eq 67, in S unknowns, the number of linearly independent solutions other than the "trivial" solution is $(S - R)$, where R is the rank of the matrix of coefficients, (see section II.A.4). In particular, if $R = S$, there is only the "trivial" null solution; also, if $S = n$ (same number of equations as unknowns), the system of equations has a solution other than the null solution if, and only if, the determinant of the matrix of coefficients is zero. The simplest case arises when $S = n$, i.e., when the total number of species involved equals the number of elementary reaction steps; physically, this corresponds to a mechanism containing one closed loop.²³⁻²⁵ Then the necessary and sufficient condition under which eq 67 has a "nontrivial" solution ($|v^*\rangle_S \neq |0\rangle_S$) for $|v^*\rangle_S$ is that the determinant $|\mathcal{V}_{nS}| = 0$. This condition is, however, guaranteed by the fact that eq 66 is known to possess a nontrivial solution for $|M\rangle_n$, so that the determinant $|\mathcal{V}_{nS}^T| = 0$; since the determinant of a matrix is equal to that of its transpose (the value of a determinant remains unaltered if its rows and columns are interchanged), a nontrivial solution must exist for $|v^*\rangle_S$. Thus, the chemical principle of detailed balance (eq 33) must be justified by some means other than mass conservation, in the case $S = n$.

A similar conclusion arises for the case $S > n$; i.e., the number of elementary reactions is greater than the number of chemical species involved; physically, this case corresponds to more than one closed loop in the mechanistic scheme. Mathematically, there are now more unknowns (S) than equations (n) in eq 67; thus, the rank of matrix \mathcal{V}_{nS} has a maximum value of n , so that there are at least $(S - n)$ linearly independent solutions for $\{v^*\}_S$, other than the null solution. Here again, each v_{γ}^* must be set to zero as the result of some additional postulate.

The final possibility is $S < n$; i.e., there are fewer elementary reactions than species involved in the mechanistic scheme, which thus has no closed loops. The maximum possible rank of the matrix \mathcal{V}_{nS} is now S ; if eq 67 is to possess *only* the null solution, then the rank of \mathcal{V}_{nS} must be this maximum value S . To prove this, note that the mass conservation condition eq 66 is known to possess a solution containing no zero values for any of the n quantities M_i (viz. the actual molecular weights). If we choose *any* $(n - S)$ of these values, and substitute them into eq 66, a nonhomogeneous system of S equations in the remaining S unknowns is obtained; this nonhomogeneous system is known to possess a solution (the remaining values of the actual molecular weights), so that the determinant of the $S \times S$ matrix must be nonzero. This is true for each and every $S \times S$ matrix formed from $(\mathcal{V}_{nS})^T$. That is to say, the rank of $(\mathcal{V}_{nS})^T$, and thus of \mathcal{V}_{nS} , is in fact S , so that eq 67 possesses *only* the "trivial" null solution $\{v^*\}_S = \{0\}_S$, which is, of course, far from trivial in fact, as it corresponds to the chemical principle of detailed balance, eq 33.

The additional postulate necessary to justify detailed balance, for mechanisms including at least one closed loop (i.e., $S \geq n$), is microscopic reversibility. This topic is discussed in some detail below.

III. Microscopic Reversibility and Detailed Balance

A. General Remarks

The physical principle of microscopic reversibility is a consequence of the "time-reversal symmetry" property of the fundamental microscopic equations of motion, believed to underlie most observable properties of matter. Far from being a mere intellectual curiosity of little practical importance, this property of time-reversal symmetry has crucial consequences, via the Onsager reciprocity theorem,³ for a wide range of non-equilibrium phenomena,²⁶ including chemical kinetics. In addition, for equilibrium properties, the Kramers degeneracy theorem²⁷⁻²⁹ is a direct result of time-reversal symmetry, and yields the prediction that the energy states of paramagnetic ions with an odd number of electrons are at least doubly degenerate. This "null Stark effect" holds in the presence of purely electric fields, whether externally applied or arising from crystal or ligand fields, and is of considerable importance for the chemistry of such ions, for their electron-spin-resonance spectra,³⁰ and for their applicability³¹ as working substances in the adiabatic demagnetization method of attaining very low temperature.

The two terms "microscopic reversibility" and "detailed balance" have become thoroughly confused, particularly in the literature of chemical kinetics; in general "detailed balance" is a result derivable from the principle of "microscopic reversibility" by appropriate averaging over one or more of the variables necessary for a complete microscopic description. For the purposes of the present article, the level of averaging, at which "microscopic reversibility" will be formally acknowledged as having been transformed to "detailed balance", will be assumed to be the level at which the theoretical variables involved are recognizable as representing *chemical* variables, i.e., mole numbers of chemical species, in the description of an elemen-

tary chemical reaction. There is clearly a degree of arbitrariness in this distinction, particularly with regard to what species are acceptably described as *chemical* species. Since both terminologies are well established in the literature, it seems important to clarify the distinction to be made between them here, however arbitrary and artificial this distinction might be.

Another question to be decided at this point concerns the level of microscopic physical theory at which to start. The following quotation from Dirac,³² concerning the status of nonrelativistic quantum-mechanics in 1929, provides a good reference point:

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

Insofar as a qualitative understanding of valency, molecular structure, and chemical reactivity is concerned, Dirac's claim has been amply fulfilled; relativistic corrections are often needed for more exact quantitative agreement with experiment to be achieved,^{33,34} and, of course, Dirac's own relativistic formulation³⁵ of quantum mechanics permits the concept of the spin angular momentum of an electron to arise from a single basic postulate, rather than as an extra assumption, tacked awkwardly on to a principal postulate; Dirac's theory³⁵ also has been claimed to offer additional *qualitative* understanding, e.g., of the problematical nodes in atomic orbitals,³⁶ although this problem is probably not a real one.

However, as emphasized by Golden³⁷ (from whose monograph the above quotation from Dirac was taken), the phenomenon of chemical (as opposed to physical) change requires considerations which are additional to, but consistent with, quantum statistics as presently developed. The difficulty basically arises from the fact that the "fundamental" particles, which are the subject of the physical description, are conserved, at least in the energy domain relevant to chemistry. This is true also of systems in chemical equilibrium, where the molecules (or ions, or atoms, etc.) may be allocated the role of the fundamental particles, and are conserved; the equilibrium statistical mechanics of chemical systems is thus a highly developed science, wherein the constraint of conservation of the numbers of molecules plays a crucial role. However, when chemical change as a function of time is considered, molecules no longer play the role of *conserved* "fundamental particles", and the quantum statistical mechanics must revert to dealing with the physical particles (electrons, protons, neutrons, etc.). The problem now is to ensure that a recognizably *chemical* description arises out of the physical theory of the time evolution of such a system;³⁷ the problem bears certain analogies to the problem of identifying theoretical quantities supposed to correspond to the macroscopic observables, temperature and entropy.

Thus, for an equilibrium system, quantum mechanics can, in principle at least, predict the allowed energies of the stationary states of the system, and can also, via the appropriate statistics, predict the relative populations of these stationary states. In some applications (e.g., spectroscopy), detailed information of this kind is what is required. However, when predictions of thermodynamic properties are required, for example, a contraction of the detailed description is necessary, and this involves further postulates additional to, but consistent with, the direct consequences of the postulates of quantum mechanics, e.g., the Boltzmann-Planck identification of the entropy, $S = k \ln \Omega$, or the identification of the Lagrangian multiplier for the system energy as $\beta = 1/kT$.

For nonequilibrium chemical systems, the quantum-mechanical equation of motion does, in principle, yield a formally complete account of the behavior of each and every atom in the system (taking the atoms as conserved in systems of chemical interest). However, chemistry is not the study of individual atoms,

but of groups of atoms (i.e., molecules); thus, the detailed description must be contracted in a particular way, so that the contracted description may reasonably be supposed to correspond to what the practicing chemist means by the chemical composition. No concise and elegant contraction analogous to the Boltzmann-Planck equation for entropy is known; clearly, the "chemical" contraction must be such as to take into account the essential "bound" character of a molecule, as distinct from a fortuitous and transitory assembly of atoms.³⁷ For chemical systems at equilibrium this problem does not arise, since the molecules themselves are taken as the (conserved) fundamental particles at the outset.

In view of these remarks, it will here be assumed that non-relativistic quantum mechanics can supply an adequate account of chemical kinetics, when suitably contracted by some scheme of chemical classification.³⁷ The primary interest of the present review lies in the so-called "time-reversal-symmetry" of the quantum-mechanical equation of motion. Since this property is shared with the classical equations of motion, the present brief discussion will begin with the classical case, and then sketch in the quantum-mechanical picture. Finally, the current status of time-reversal-symmetry, in the quantum electrodynamics of fundamental physical particles, will be briefly indicated.

B. Time-Reversal Symmetry and Microscopic Reversibility

The title of this section was chosen to suggest that the general topic involves a *mathematical* property of the equations of motion. It will suffice, for present purposes, to consider the Newtonian (classical) equation of motion for a particle of mass m , in one dimension x :

$$F(x) = (d/dt)(m dx/dt) \quad (68)$$

where $F(x)$ is the force acting in the x direction, and t is a time variable. Since the time differentiation is performed twice, the differential elements may be either $+dt$ or dt' , where $t' \equiv -t$, without affecting the equation. It is this property of the equations of motion which is referred to as time-reversal symmetry; generalized classical equations of motion (Lagrangian or Hamiltonian) also possess this property.

It seems worthwhile to include here a brief comment on the facile transposition of $+t$ into $-t$, mentioned above. This should not necessarily be taken to mean that "time runs backwards". In fact, the only consequences of the time-reversal symmetry of eq 68, which appears to have any meaningful physical content, involves "one-way time"; a detailed discussion of this, and other varied aspects of the concept of time, may be found elsewhere³⁸⁻⁴⁰ and is briefly touched on below.

Before doing so, however, it is appropriate to discuss here the nonrelativistic quantum-mechanical equation of motion in the Schrödinger representation (wherein all explicit time dependence is carried by the wave function), written as:

$$i\hbar(d\Psi/dt) = H\Psi \quad (69)$$

where Ψ is the state wave function. For simplicity, we shall consider only cases where spin variables are not important though, in fact, the treatment is not too complicated when spin is included.^{29,44,45} Then, for two particles A and B, the Hamiltonian will have the form:

$$\mathcal{H}(\mathbf{p}_A, \mathbf{p}_B, \mathbf{r}_A, \mathbf{r}_B) = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} + V(\mathbf{r}_A, \mathbf{r}_B) \quad (70)$$

where $\mathbf{p}_A = (\hbar/i)\nabla_A$ is the vector operator for all momentum variables pertinent to particle A. It is clear that, if eq 69 is simply transformed by ($t \rightarrow -t$), the resulting equation is *not* the same. However, if we then apply the complex conjugation operator C to both sides of the "time-reversed" version of eq 69 (thus reversing the momentum vector operators), we obtain:

$$C\{i\hbar[d\Psi(-t)/d(-t)]\} = -i\hbar[d\Psi^*(-t)/d(-t)] \\ = i\hbar[d\Psi_{\text{rev}}/dt] \quad (71)$$

$$C\{H\Psi(-t)\} = H^* \Psi^*(-t) = H\Psi_{\text{rev}}$$

where $\Psi_{\text{rev}} \equiv \Psi^*(-t)$, and $H = H^*$ because of the dependence of H^* on $(\mathbf{p})^2$. Clearly, if Ψ is a solution of eq 69, so is Ψ_{rev} ; this is then the quantum-mechanical analogue of the time-reversal symmetry property of the classical equations of motion, discussed above.

Elucidation of the physical consequences of these symmetry properties of the equations of motion is, of course, rather different for the classical and quantum-mechanical cases. A rather complete discussion of the classical case has been given by Schlegel,³⁸ this may be briefly summarized by saying that the physically meaningful consequence of the time-reversal symmetry property of eq 68 is that, for any classical trajectory which satisfies eq 68, there exists an equally acceptable trajectory related to the first via "path reversibility", in the following sense: if a system with positions and velocities (x_i, \dot{x}_i) at $t = t_0$ undergoes a trajectory satisfying eq 68 such that at $t = t_0 + \Delta t$ the positions and velocities are (x_f, \dot{x}_f) , then this system will, if given initial conditions $(x_i, -\dot{x}_i)$, proceed to a final state $(x_f, -\dot{x}_f)$ after the same positive time interval Δt . The second motion is related to the first by the familiar analogy of a motion picture film run backwards. For the special case of a collision between two particles, the two motions correspond to Tolman's⁴³ "inverse collisions".

In quantum mechanics it is not possible to discuss the motion in terms of a trajectory, i.e., an exact specification of all coordinates and momenta at all times. Rather, the discussion must necessarily revolve around probabilities of observing a system in a specified state; the quantum-mechanical analogy to the classical path-reversibility property described above may be formulated somewhat as follows.

Let w be the probability of observing the system, at time ($t_0 + \Delta t$) in a certain state ϕ , when it was prepared at an earlier time t_0 in the pure state Ψ , i.e., in a state for which all dynamical variables are known; let w_{rev} be the probability of finding the system, at time ($t_0 + \Delta t$), in the state Ψ_{rev} when it was prepared in the state ϕ_{rev} at time t_0 . Then, it is possible to show,⁴⁴ as a general consequence of eq 71, that $w = w_{\text{rev}}$. Although this proof is not difficult,⁴⁴ it does require considerable recapitulation of definitions and notation and will not be transcribed here.

This proof of the equality of transition probabilities does not yet constitute a proof of path reversibility unless it can be shown that the differences between Ψ and Ψ_{rev} , for example, lead to no differences in the concomitant predictions of observable quantities, other than a change in sign for the momenta. Again, a complete rigorous proof of this result⁴⁴ is too long to be included here.

As a simple special case, and with a view to the ultimate chemical application of the present discussion, the collision of two free particles will be considered. In the quantum-mechanical treatment, probabilities of transition between stationary states of the free particles are considered, and it may no longer be assumed that a coordinate (e.g., x) and its conjugate momentum (e.g., mx) may be simultaneously specified exactly. Then, since the situation of interest concerns the collision of two free particles (i.e., before and after the collision, the two particles do not interact significantly with one another), it seems sensible to concentrate on the *momenta* in the initial and final states, since the positions are of little or no importance when the particles are far enough apart that they do not interact. That is, we describe these states in the momentum representation, rather than the configuration representation more familiar in quantum chemistry. Thus, we seek the following relationship between the transition probabilities:

$$w[(\mathbf{p}_A, \mathbf{p}_B) \rightarrow (\mathbf{p}'_A, \mathbf{p}'_B)] \\ = w_{\text{rev}}[(\mathbf{p}'_A, \mathbf{p}'_B) \rightarrow (\mathbf{p}_A, \mathbf{p}_B)] \quad (72)$$

Equation 72 is the quantum-mechanical statement of path reversibility under momentum reversal, for the collision of particles A and B, if spin variables are not relevant; \mathbf{p}_A , for example, denotes all momenta relevant to particle A before the collision, and \mathbf{p}_A' the corresponding values after the collision. Similarly, \mathbf{p}_A^- denotes a state identical with that described by \mathbf{p}_A , but with all momenta reversed. In the case where spin variables are relevant, they must also have their directions reversed^{44,45} in the specification of the inverse collision. The proof of eq 72 is most easily done using time-dependent perturbation theory⁴⁵ for the present special case of the collision of free particles (molecules).

Thus, nonrelativistic quantum mechanics, and its classical limit, predict path reversibility under momentum reversal, as a consequence of symmetry properties of the equations of motion. (Dirac's relativistic equation of motion³⁵ for a particle of spin $\frac{1}{2}$ in a nonquantized field also is invariant under a suitably defined time-reversal operation.) As a final comment in this section, it seems appropriate to mention the current activity concerning time reversal in fundamental particle physics. Central to this controversy is the famous CPT theorem;⁴⁶ the status of this theorem is such that it appears to be impossible to formulate equations of motion in quantum electrodynamics, consistent with the special theory of relativity, which do *not* possess CPT symmetry.⁴⁷⁻⁴⁹ In addition, all experimental tests so far conducted appear to be in accord with the theorem; a simple statement of the theorem might be: "Every relativistic quantum field theory is invariant under the consecutive reversals of charge (C), space (parity P) and time (T)".

Although quantum electrodynamics seems rather remote from the nonrelativistic Schrodinger equation (eq 69), here assumed to offer an ultimate theoretical basis for chemical kinetics, the fact that T symmetry *alone* is *not* guaranteed by the CPT theorem raises the question of the universal validity of microscopic reversibility, in the present sense. The spectacular overthrow of parity^{50,51} is well known; more recently⁵² experiments indicating a breakdown of combined CP symmetry have been carried out. While the evidence for the breakdown of CP symmetry is not as clearcut and direct as that indicating the P-symmetry breakdown (constituting a deviation of a fraction of a per cent from the CP-symmetry prediction), this result is of great significance; either CPT invariance is to remain intact, and breakdown of CP symmetry must imply a concurrent breakdown of T symmetry, or else the CPT theorem is not exact. As a result, considerable effort has been expended⁴⁹ on efforts to find direct evidence of the breakdown of T symmetry; thus far, however, no such evidence has been found.

Even if it were to be found, the implications for the role of time symmetry in *chemistry* would probably be minimal. To see this, it should be appreciated that modern physics recognizes four distinct fundamental forces; these are gravity, the "strong" nuclear interaction force, the so-called "weak" interaction force responsible for the decay of elementary particles, and the electromagnetic force between charged particles. The violations of P symmetry and of CP symmetry (with its implication for T symmetry) have all been observed in cases where the "weak" interaction force was operative; chemistry involves only the electromagnetic force, for which the validity of T symmetry does not appear to be in question at present.⁵³ Thus, the Hamiltonians relevant to chemical problems are such that P and T symmetry *are* valid; an ingenious application of these principles to the chemical problem of optical activity is due to Barron.⁵⁴

C. Detailed Balance in Chemical Kinetics

1. Reversible and Irreversible Processes

The time-reversible symmetry of the equations of motion leads to the physical prediction that any completely specified mechanical event, and its momentum-reversed counterpart, cor-

respond to equally acceptable solutions of the equations; however, it is a matter of observation that chemical reactions do *not* proceed with equal facility in either direction. Nonetheless, every molecular collision resulting in "chemical" changes and its momentum-reversed counterpart are equally valid consequences of the equations of motion. This is simply an example of the general problem of reconciling microscopic reversibility with macroscopic irreversibility;⁴³ in general terms, the resolution of this apparent paradox requires the realization that the reversible laws of motion refer to precisely defined mechanical states, while the macroscopic observations correspond to situations where this precise information is lacking. The concept may be reexpressed in a possibly more useful fashion by noting that, in a normal experiment in chemical kinetics, the observations correspond to a large-scale averaging of detailed molecular events. Although the transition probabilities for precisely defined "forward" and "reverse" chemical transformations are equal, in accordance with the equations of motion, the *numbers* of "forward" and "reverse" collisions, arising naturally in the reaction mixture, are *not* equal, so that the observable averages are not equal either. This idea will be made more explicit later, and is included here to indicate that spontaneous, irreversible chemical change is subject to the same general analysis as simpler physical processes.⁴³

It seems appropriate here to attempt to clarify some possible confusion in terminology, with regard to the meaning of "reversible" and "irreversible" reactions in chemistry. In the sense discussed above, *all* chemical reactions are irreversible, in that no chemical system spontaneously proceeds from its equilibrium state to some nonequilibrium state (other than small statistical fluctuations). The term "reversible reaction", or "kinetically reversible reaction", in its everyday colloquial use by chemists, however, merely implies that the equilibrium state involves appreciable concentrations of both "reactants" and "products"; thus, by suitable choice of initial conditions, the reaction may be induced to proceed with net increase of *either* "reactants" or "products". In the same colloquial sense, an "irreversible" reaction is such that the concentration of "reactant", for example, in the equilibrium state, is sufficiently small to be undetectable; in practical terms, therefore, it is impossible to arrange boundary conditions which permit a net conversion of (product \rightarrow reactant) to be observed. The situation is further confused by the use of the same words in a thermodynamic sense. It is quite possible to carry out an "irreversible" chemical reaction (in the colloquial sense) in a "reversible" fashion (in the thermodynamic sense), for example, by using a suitable electrochemical cell externally balanced by a potentiometer. While it is true that all three senses of the terms are closely related, they are clearly not identical in all respects.

2. Stochastic Model for Chemical Reaction

It is the aim of this section to show how the physical principle of microscopic reversibility leads to the chemical principle of detailed balance (eq 33) for all cases, including chemical mechanisms with closed loops. Such demonstrations already exist in the literature, the most famous of which is that due to Onsager,³ although an intuitive understanding of the principles involved can be found in the earlier work of Lewis.⁶⁰ A more recent derivation,⁶² based upon scattering theory and the Boltzmann collision equation, is due to Light, Ross, and Shuler; this latter work⁶² is of direct relevance to modern chemical dynamics as studied by molecular beam techniques, for example. Each of these derivations^{3,62} is complete, provided one is content to accept the "local equilibrium" theory of chemical kinetics; this theory is based upon the assumption that the internal states of reactant molecules can be described by the equilibrium distribution function. Thus, Onsager³ took no account of entropy production due to equilibration of internal modes,

thereby implicitly assuming them to be unperturbed by the chemical reaction; Light, Ross, and Shuler quite explicitly obtained⁶² theoretical expressions for rate constants by appropriate averaging over equilibrium distribution functions for the internal modes.

The justification for including yet another discussion of this topic in the present work is that some of the more interesting *experimental* findings regarding detailed balance have involved conditions in which the local equilibrium hypothesis is almost certainly invalid; these are discussed in section IV below. At least one of these cases (the $\text{H} + \text{Cl}_2 \rightleftharpoons \text{HCl} + \text{H}$ system) is qualitatively inexplicable in terms of local equilibrium theories of chemical kinetics. Thus, the present work will concentrate on a discussion of how the chemical principle of detailed balance arises from microscopic reversibility in nonequilibrium theories of chemical kinetics. A physical model for a simple reaction will be presented, simple enough that the aspects of importance for the present work may be considered without irrelevant encumbrance. The chemical reaction is an elementary isomerization reaction, proceeding via collisions with an inert collision partner Z (e.g., argon), assumed to have no internal degrees of freedom, and to be present in large excess:



It is worth emphasizing at this point that the reaction described by eq 73 will be assumed to be reversible in the colloquial sense, i.e., the equilibrium constant is not too different from unity. The large excess of Z ensures that the temperature remains essentially constant, and that each binary collision involves at least one Z; the latter condition will permit the use of a set of linear equations to describe the physical model for this reaction. The reactive molecule, chemically recognizable as either isomer A or B (e.g., cis or trans form of a suitable olefin), is supposed to possess n internal stationary states; further, it is supposed that these states may be enumerated in such a way that states 1 to $(m - 1)$ inclusive may be assigned to isomer A, and the remainder to B.

It is at this point that the difficulties of the imposition of chemistry, on to the physical description, arise. In the present example of a reaction in an ideal gas system, these difficulties are minimized since the complete-system wave function may be built up from single-molecule functions. However, even here the assignation of molecular states to chemical species is not without ambiguity.^{55,56} For example, consider the well-known theories of unimolecular decomposition. That due to Slater⁵⁷ assumes that the conversion from reactant to product has occurred when the relevant vibrational mode has acquired a critical amplitude; that is, Slater's criterion for assigning chemistry to the physical description is based upon configurational properties. On the other hand, the theory associated with the names of Rice and Ramsperger⁵⁸ and Kassel⁵⁹ uses a criterion based upon the energy concentrated in the critical mode. Transition state theory⁶⁰ distinguishes between reactants and products using criteria based upon both energy and configuration. For reactions in condensed media, the problem is considerably more complex.³⁷ However, for present purposes, it will be assumed that the n internal states of the reacting molecule may be assigned, in a chemically meaningful fashion, to isomers A and B; this point will become more critically important when a reaction more complicated than eq 73 is considered. In view of the discussion in section III.A above, it seems worthwhile to emphasize here that choice of an isomerization reaction, as a model for discussion, avoids the worst problems of the "boundness" criterion³⁷ for chemical classification of the physical description of the atoms. The chemical change considered is thus simply a change in the fashion in which a given set of atoms are bound together; nonetheless, as will become clear later, a certain degree of arbitrariness remains in the assignation of physical states to chemical species.

The time evolution of the physical model may be described using the transition probabilities of eq 72, which are deduced from the equation of motion, eq 69. However, in the usual chemical kinetics experiment, the detailed microscopic specifications implicit in eq 72 are irrelevant; usually the details of each and every individual collision are not known, although experiments in crossed molecular beams do require at least some detail in the description. Since the establishment of the equilibrium Maxwellian distribution of velocities in a gas is established on a much faster time scale than either relaxation of internal modes or than chemical reaction, it is usually⁶¹ an excellent approximation to average the microscopic transition probabilities over this Maxwellian velocity distribution. The details of this averaging are clearly explained elsewhere,⁶² for present purposes, it will suffice to note that the detailed transition probabilities per collision, the w 's of eq 72, are thereby transformed into k_{ij} 's, transition probabilities per unit time, relating transitions between the completely specified (unit degeneracy) internal states i and j . Microscopic reversibility as contained in eq 72 is thereby transformed⁶² to:

$$k_{ij}(T)/k_{ji}(T) = (\mu/\mu')^{3/2} \exp[-(\epsilon_j - \epsilon_i)/kT] \quad (74)$$

where $(\epsilon_j - \epsilon_i)$ is the internal energy difference between states j and i , while μ and μ' are the reduced masses for reactants and products, respectively. In the present example of an isomerization reaction, eq 73, clearly $\mu = \mu'$, so that eq 74 is thereby simplified to include the exponential term only. For present purposes, since the averaging has not yet reached the chemical level, eq 74 will still be referred to as microscopic reversibility.

The time evolution of the physical description, using the k_{ij} 's, is now assumed to be given by an appropriate "master equation" rather than the more fundamental quantum-mechanical equation of motion, eq 69; the applicability of this approach is a matter of serious concern,^{55,63,64} but it will here be assumed that the necessary conditions are fulfilled. The k_{ij} coefficients are averaged quantum-mechanical transition probabilities and may be used to describe a "stochastic process" or "Markov chain"; these latter two terms are mathematical jargon, which in the present context correspond to a "master equation", or equation of motion expressed in terms of transition probabilities.

The concept of a Markov chain⁶⁵ provides a mathematical model for a system whose state changes with time t according to some probability law, in such a manner that the probability of the system going from a given state j at t_0 , to a state i at time $(t_0 + \Delta t)$, is *independent* of the states of the system at times prior to t_0 (the interval Δt is supposed small enough that the chance of more than one transition occurring within Δt is very small). This "no-memory" feature of a Markov chain clearly corresponds to an essential feature of quantum-mechanical transition probabilities.

The application of Markov chains, and stochastic principles in general, to chemical problems has been extensively reviewed by McQuarrie.⁶⁶

For present purposes, it is sufficient to note that the predictions of stochastic theories involve means and variances of relevant quantities, as expected from the initial description in terms of transition *probabilities*. However, it turns out⁶⁵⁻⁶⁷ that the predicted expectation values for the populations of the internal states i, j , etc., are identical with the precise predictions obtained if the k_{ij} are treated as deterministic rate constants for the physical change of state $i \rightarrow j$. Thus, the theory of stochastic processes bears a relationship to chemical kinetics similar to that borne by statistical mechanics to thermodynamics.⁶⁶ In these terms the success of the deterministic kinetic approach is to be explained by the fact that, for reasonably large systems, statistical fluctuations about the mean expectation values are very small compared with experimental uncertainties. In what

follows, the deviations from the means will be ignored, and the deterministic approach adopted.

3. Solution of Deterministic Multilevel Model for Two-Species Isomerization

The simple model reaction given by eq 73 contains no closed loops in its chemical mechanism; thus, detailed balance in this case can be justified on purely macroscopic grounds. The following analysis thus serves to establish the general approach; treatment of a simple closed-loop mechanism will then follow. The multilevel master equation in the deterministic limit becomes:

$$dx_i/dt = \sum_{j=1}^n (k_{ij}x_j - k_{ji}x_i); 1 \leq i \leq n \quad (75)$$

where $k_{ii} = 0$, and x_i is assumed to be a continuous variable, giving the fractional population per unit volume of molecules in internal state i (again, as in section II, the discussion is restricted to constant volume systems). Also for convenience, the concentration of Z has been included in the k_{ij} , which are now equivalent to pseudo-first-order rate constants describing the rates of $i \rightarrow j$ transitions. The n -coupled differential equations described by eq 75 may be written as a single matrix equation:

$$(d/dt)x(t) = -Kx(t) \quad (76)$$

where $x(t)$ is a column vector whose i th element is x_i , K is a transport matrix, with $K_{ij} = \sum k_{ij}$, and $K_{ji} = -k_{ji}$.

The properties of the matrix K , and the solution of eq 76, are well documented⁶⁸⁻⁷² and are sketched in Appendix A; the solution is merely stated here:

$$x_i(t) = x_i^* + \sum_{r=2}^n [c_r^0 \phi_r(i) \exp(-\lambda_r t)] \quad (77)$$

$$1 \leq i \leq n$$

$\phi_r(i)$ is the i th element of the r th eigenvector of K , and λ_r is the corresponding eigenvalue; as a consequence of mass conservation in a closed system, one eigenvalue is zero, λ_1 say. The other eigenvalues are real and positive, as a direct consequence⁶⁸⁻⁷² of microscopic reversibility, eq 74. The c_r^0 are coefficients dependent on the initial boundary conditions $x(0)$, and x_i^* is the infinite-time-limit (equilibrium) value of x_i . Thus, eq 77 is the solution to the physical model for the chemical reaction (eq 73), in the deterministic limit; the description is still "physical", in that no recognizable *chemical* concentrations appear in eq 76 and eq 77.

The phenomenological description of this chemical reaction would involve a simple rate equation of the form:

$$-da/dt = db/dt = ka - k'b \quad (78)$$

where a is the fraction of the total concentration which is isomer A, and b the fraction which is B; eq 78 is simply the usual rate equation, with both sides divided by the (constant) total concentration of A plus B. The rate constants k and k' are functions of temperature only, independent of time and of the initial conditions of the particular experiment, as discussed in section II above. For convenience, the concentration of Z has been included in k and k' also; the orders of reaction have been assumed to be exactly unity, in accordance with normal practice in experimental kinetics where empirical orders close to integral values are set to those integers. At this point, it should be noted that the detailed physical mechanism of the model reaction contains no "spontaneous" steps which proceed without the intervention of a collision; the reaction will thus be truly second order at all pressures, with none of the fall-off behavior typical of many "unimolecular" reactions.^{73,74}

The problem now resolves itself into discovering the conditions under which the physical solution (eq 77) is consistent with the phenomenological chemical description (eq 78). The first step must clearly be to impose chemical classifications upon the physical description; then the theoretical constructs, supposed to correspond to the empirical quantities in eq 78, are assumed⁷¹ (see discussion following eq 73), to be:

$$a \equiv \sum_{i=1}^{m-1} x_i = a^* + \sum_{r=2}^n \left[c_r^0 \exp(-\lambda_r t) \left(\sum_{i=1}^{m-1} \phi_r(i) \right) \right] \quad (79)$$

$$b \equiv \sum_{i=m}^n x_i = b^* + \sum_{r=2}^n \left[c_r^0 \exp(-\lambda_r t) \left(\sum_{i=m}^n \phi_r(i) \right) \right]$$

$$= b^* - \sum_{r=2}^n \left[c_r^0 \exp(-\lambda_r t) \left(\sum_{i=1}^{m-1} \phi_r(i) \right) \right] \quad (80)$$

$$-da/dt = \sum_{r=2}^n \left[c_r^0 \lambda_r \exp(-\lambda_r t) \left(\sum_{i=1}^{m-1} \phi_r(i) \right) \right] \quad (81)$$

The second form of writing eq 80 arises from a property⁶⁹⁻⁷¹ of the matrix K , whereby for $\lambda_r \neq 0$, $\sum_{i=1}^n \phi_r(i) = 0$. If now conditions are sought under which the two descriptions are exactly consistent, eq 79-81 should be substituted into eq 78, to give:

$$\sum_{r=2}^n \left[c_r^0 \lambda_r \exp(-\lambda_r t) \left(\sum_{i=1}^{m-1} \phi_r(i) \right) \right] \equiv (ka^* - k'b^*)$$

$$+ (k + k') \sum_{r=2}^n \left[c_r^0 \exp(-\lambda_r t) \left(\sum_{i=1}^{m-1} \phi_r(i) \right) \right] \quad (82)$$

Equation 82 is an identity in the sense that it must hold for all times t and all initial conditions $\{c_r^0\}$, where k and k' are independent of these quantities. The two conditions for the identity to hold *exactly* are clearly:

$$k/k' = b^*/a^* = K^* \quad (83)$$

$$\lambda_r = (k + k') \quad \text{or} \quad \sum_{i=1}^{m-1} \phi_r(i) = 0, 1 < r \leq n \quad (84)$$

While it is encouraging that eq 83 is the appropriate detailed balance relationship, the physical implications of eq 84 may be shown⁷⁵ to be so demanding that it is doubtful that they would be fulfilled in any special example, and certainly not in general. Thus, it is unrealistic to insist upon obtaining the phenomenological rate equation (eq 78) as an *exact* consequence of the physical model, and approximate solutions must be sought.

The traditional approach has been to make what has been here referred to as the "local equilibrium" assumption; such an assumption is common to many reaction rate theories, including transition-state theory,⁶⁰ and invariably yields the chemical principle of detailed balance as a fairly direct consequence of microscopic reversibility.^{3,62} In the present simple model, the assumption implies that states 1 to $(m-1)$ inclusive are equilibrated among themselves, as are states m to n inclusive; the nonequilibrium break is thus assumed to fall sharply between states $(m-1)$ and m . The approximation may be expressed by:

$$x_i(t)/a(t) = x_i^*/a^*$$

$$= \left[\exp(-\epsilon_i/kT) / \sum_{i=1}^{m-1} \exp(-\epsilon_i/kT) \right] \quad (85a)$$

for $1 \leq i \leq m-1$

$$x_j(t)/b(t) = x_j^*/b^*$$

$$= \left[\exp(-\epsilon_j/kT) / \sum_{j=m}^n \exp(-\epsilon_j/kT) \right] \quad (85b)$$

for $m \leq j \leq n$

The local equilibrium approximation to the rate constants are then:

$$k_E = \sum_{i=1}^{m-1} \left[(x_i^*/a^*) \left(\sum_{j=m}^n k_{ij} \right) \right]$$

$$k_E' = \sum_{j=m}^n \left[(x_j^*/b^*) \left(\sum_{i=1}^{m-1} k_{ji} \right) \right] \quad (86)$$

By substituting in these expressions from eq 85, some straightforward algebra shows that k_E and k_E' obey the detailed balance relation as a result of microscopic reversibility, eq 74.

This is reasonably satisfactory, and the extent of the errors introduced by the approximation is discussed below; however, taking a general point from conventional chemical kinetics, an approximate solution of the "stationary state" type is normally of wider applicability than the corresponding equilibrium approximation. Such an approximate solution may be obtained from eq 82 by noting that, for most situations appropriate to the present chemical reaction, the nonzero eigenvalues of K may be ordered in such a way that:

$$0 = \lambda_1 \approx \lambda_2 \ll \lambda_3 < \lambda_4 < \dots < \lambda_n \quad (87)$$

(Note that this numbering of the eigenvalues does not correspond in any way to that of the internal states, eq 73). Justification for eq 87 will be discussed below; for the present, the implications for eq 82 are such that, after a short "incubation time" or "induction period", of the order of λ_3^{-1} , the exact eq 82 will be well approximated by a form where all terms with $r > 2$ are ignored. For convenience, this approximation will be referred to as the "eigenvalue approximation"; the corresponding theoretical approximation to the rate constants will then be given by the appropriate forms of eq 83 and eq 84:

$$k_\lambda/k_\lambda' = K^* \quad (88)$$

$$k_\lambda + k_\lambda' = \lambda_2 \quad (89)$$

That this solution corresponds to a steady-state assumption, of a special sort, may be seen from eq 82 with terms in $r > 2$ omitted; for any i and j , this gives:

$$(x_i(t) - x_i^*)/(x_j(t) - x_j^*) = \phi_2(i)/\phi_2(j) \quad (90)$$

The more conventional steady-state assumption in chemical kinetics would have postulated the approximate constancy of (x_i/x_j) ; as shown by eq 90, however, this quantity *does* vary with time in the eigenvalue approximation, and the time-independent quantity is more complicated. Nonetheless, by analogy with conventional kinetics, it is to be expected that the eigenvalue approximation would be acceptable over a wider range of conditions than its local equilibrium counterpart; this question is also discussed further below. In addition, using the same analogy, the eigenvalue approximation should yield the local equilibrium result in the limit where the k_{ij} 's appropriate to internal relaxation are very much larger than those appropriate to chemical isomerization. This has been shown by Snider,⁷¹ in an elegant fashion, by writing the complete transport matrix K as the sum of two matrices ($K_r + K_c$); K_r contains only those k_{ij} 's relevant to relaxation, and K_c those relevant to chemical reaction. By treating K_c as a perturbation upon K_r , expressions for k_λ and k_λ' were obtained in which the leading terms were k_E and k_E' , respectively; the perturbation terms⁷¹ become smaller as K_c is made less and less important relative to K_r , in accordance with the intuition outlined above.

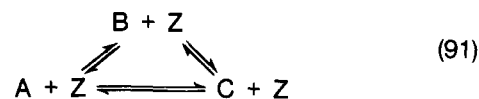
Related to this view of the eigenvalue approximation as a steady-state solution is the interpretation of the rate constants k_λ and k_λ' ; as evident from eq 80 and eq 89, each is a simple fraction of λ_2 , which in turn is a complex function of *all* the k_{ij} 's, including those for chemical transitions in *both* directions, and for internal relaxation of *both* species. Thus, as emphasized by Widom,⁷² there is *no* justification for regarding the terms (ka) and $(k'b)$ as the "forward" and "reverse" reaction rates, re-

spectively; only if the local-equilibrium limit (eq 86) is applicable is such an interpretation acceptable (see section II.A.1).

In both the local equilibrium and the eigenvalue approximations, the detailed balance relationship arose quite naturally. However, this does not contribute anything further to our understanding of detailed balance, over and above the purely phenomenological discussion in section II, since the chemical mechanism considered (eq 73) does *not* contain a closed loop; thus, in the model thus far, the emergence of detailed balance is simply a consistency check. The model must now be extended to closed-loop mechanisms, and the simplest conceivable example of such a mechanism will next be treated.

4. Solution of Model for Triangular Isomerization Reaction

The simplest closed-loop chemical mechanism, consistent with the present stochastic model, is:



The phenomenological rate description now involves two independent rate equations:

$$-da/dt = (k_{AB} + k_{AC})a - k_{BA}b - k_{CA}c \quad (92a)$$

$$-db/dt = -k_{AB}a + (k_{BA} + k_{BC})b - k_{CB}c \quad (92b)$$

$$-dc/dt = -k_{AC}a - k_{BC}b + (k_{CA} + k_{CB})c \quad (92c)$$

Any two of eq 92 may be chosen as the independent set.

The theoretical model is unchanged, except that it must now be assumed possible to classify the n states into *three* groups, corresponding to the chemical species A, B, and C, such that:

$$a = \sum_{i=1}^{l-1} x_i; \quad b = \sum_{i=l}^{m-1} x_i; \quad c = \sum_{i=m}^n x_i \quad (93)$$

The solution eq 77 still applies; in addition, exact consistency of this theoretical model with eq 92, while feasible mathematically, again carries physical implications so stringent as to render the necessary conditions quite impossible.⁷⁷ Local equilibrium approximations to the rate constants, entirely analogous to those for the two-isomer case (eq 86), may be constructed and demonstrated to fulfill detailed balance as a direct consequence of microscopic reversibility:

$$k_{AB}^E/k_{BA}^E = b^*/a^* = K^*_{AB}, \text{ etc.} \quad (94)$$

Evaluation of theoretical approximations to the rate constants for the reaction described by eq 91, in terms of the eigenvalue assumption, requires that the *three* smallest eigenvalues now be included, to account for the *three* species:

$$0 = \lambda_1 \approx \lambda_2 \approx \lambda_3 \ll \lambda_4 < \lambda_5 < \dots < \lambda_n \quad (95)$$

The justification for conditions like eq 87 and eq 95 is closely connected with the feasibility of classifying the n physical states into the appropriate number of chemical species (eq 79, 80, and 93), and is described below. Application of eq 93 and eq 95 to the general solution, eq 82, gives the following six conditions for consistency of the phenomenological description (eq 92) with the eigenvalue approximation:⁷⁷

$$[k_{AB}^\lambda(k_{CA}^\lambda + k_{CB}^\lambda) + k_{CB}^\lambda k_{AC}^\lambda] / [k_{BA}^\lambda(k_{CA}^\lambda + k_{CB}^\lambda) + k_{BC}^\lambda k_{CA}^\lambda] = b^*/a^* = K^*_{AB} \quad (96a)$$

$$[k_{BC}^\lambda(k_{AB}^\lambda + k_{AC}^\lambda) + k_{BA}^\lambda k_{AC}^\lambda] / [k_{CB}^\lambda(k_{AB}^\lambda + k_{AC}^\lambda) + k_{AB}^\lambda k_{CA}^\lambda] = c^*/b^* = K^*_{BC} \quad (96b)$$

$$k_{CA}^\lambda - k_{BA}^\lambda = (\lambda_3 - \lambda_2)\omega_2\omega_3/(\omega_2 - \omega_3) \quad (96c)$$

$$k_{CB}^{\lambda} - k_{AB}^{\lambda} = (\lambda_3 - \lambda_2)/(\omega_3 - \omega_2) \quad (96d)$$

$$k_{AB}^{\lambda} + k_{AC}^{\lambda} + k_{CA}^{\lambda} = (\omega_3\lambda_3 - \omega_2\lambda_2)/(\omega_3 - \omega_2) \quad (96e)$$

$$k_{AB}^{\lambda} + k_{BA}^{\lambda} + k_{BC}^{\lambda} + k_{CB}^{\lambda} + k_{CA}^{\lambda} + k_{AC}^{\lambda} = \lambda_2 + \lambda_3 \quad (96f)$$

In eq 96, $u_r = \sum_{i=1}^{r-1} \phi_r(i)$, $v_r = \sum_{i=1}^{m-1} \phi_r(i)$, $z_r = \sum_{i=m}^n \phi_r(i)$, and $\omega_r = u_r/v_r$, for $r = 2$ or 3 ; recall that for $r \geq 2$, $(u_r + v_r + z_r) = 0$.

Equations 96a and 96b are familiar^{3,81} as the restrictions imposed by thermodynamics *alone* upon the rate equations, eq 92; they are consistent with detailed balance, but do not themselves require detailed balance; i.e., eq 96a and eq 96b give a necessary, but not sufficient, condition for detailed balance. Further, it may be shown⁷⁷ that eq 96c-f do *not* provide the extra conditions necessary to reduce eq 96a and 96b to detailed balance. Although microscopic reversibility has been built into the theory (and requires that the eigenvalues be real-valued), detailed balance does *not* emerge naturally from the eigenvalue approximation, as contained in eq 96.

It is at this point that the classification of physical states into chemical species, the nature of the eigenvalue spectrum (eq 87 and 95), and the justification of detailed balance as a consequence of microscopic reversibility may be simultaneously clarified by an approach due to Widom,^{82,83} and to the present author.^{77,85} The basis of Widom's idea^{82,83} is to reduce a rather special, but physically realistic, case of the stochastic model to a form which is closely analogous to a Schrodinger equation relevant to a familiar problem in quantum chemistry; many properties of the latter solution are well investigated, and the formal analogy with the kinetic equations permits considerable clarification of the latter. Widom's procedure is described in some detail in Appendix B, but the more descriptive exposition in the main text is intended to convey the main ideas without too much mathematical distraction.

The first step is to replace the discrete index of states used here (i or j) with a continuous index (x or y); the internal states of polyatomic molecules are, in fact, extremely numerous, and this seems entirely justifiable. Then, the summations appearing in the present treatment will be replaced by appropriate integrals, the composition vector $|x_i\rangle$ by a composition function, and the transition matrix K by a corresponding transition kernel. The general analysis may now proceed exactly as for the discrete case (see Appendix B).

Reduction of the general model to the special quantum-mechanical analogy now requires that the averaged transition probabilities $\omega(x,y)$ (cf. k_{ij} in the discrete treatment) are significant for $y \approx x$ only. Up to this point, x (or i) has been a somewhat arbitrary label for the physical states; now, however, this restriction upon $\omega(x,y)$ requires more careful examination of x . The physical model for the chemical reaction involves collision of a structureless atom Z (e.g., argon) with the reactant molecule; in such a case, small energy transfers are more probable than large transfers. The Landau-Teller transition probabilities for relaxation of a harmonic oscillator⁷⁶ give a possibly extreme example of this principle. Thus the above restriction upon the $\omega(x,y)$ is physically reasonable provided that the index x is chosen to be a smoothly varying function of the internal energy of the reactant.

Figure 1 is a sketch of a typical potential energy diagram for the two-isomer case which for simplicity's sake is the only case considered in detail here; θ is the progress variable⁸⁴ (e.g., twisting angle of the π bond of an olefin). The division between isomers A and B, to be in accord with chemical intuition, must clearly be drawn somewhere near the energy maximum; the assignment of states above this maximum seems completely arbitrary, but their equilibrium populations will be extremely small. This point becomes important later. The continuous index of states x is chosen to run from $-\infty$ to $+\infty$ for purposes of the analogy with quantum chemistry. (It is clear that x and θ , while

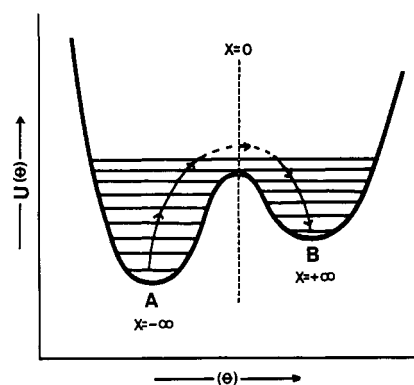


Figure 1. Diagram of potential energy vs. progress variable θ for simple two-species isomerization. The continuous variable x is an index for the internal state (see text).

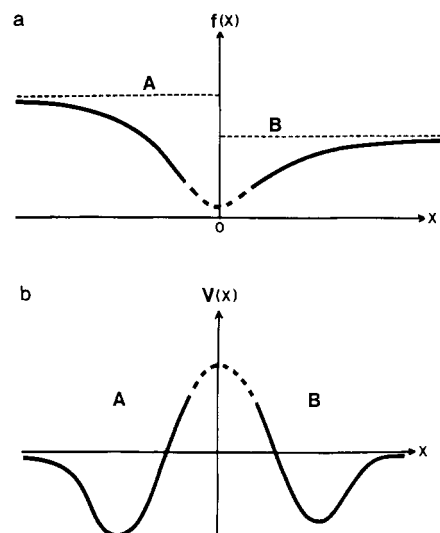


Figure 2. (a) Plot of Boltzmann distribution function $f(x)$ vs. x (label for internal states), corresponding to potential energy diagram shown in Figure 1. (b) Sketch of $V(x) \sim (\sqrt{f(x)})' / \sqrt{f(x)}$, corresponding to Figure 2a (see text).

related, are *not* identical; for example, there are normally two "classical turning-point" values of θ for each value of x .)

Then, as shown by Widom⁸² (see also Appendix B), the eigenvalue equation for the *symmetrized* transition kernel (cf. Appendix A) of the appropriate master equation may be reduced to:

$$-\frac{1}{2}M_2\psi'' + \frac{1}{2}M_2[(\sqrt{f})'/\sqrt{f}]\psi = \lambda\psi \quad (97)$$

$\psi(x)$ and λ are the eigenfunction and eigenvalue, respectively, of the transition kernel; primes denote differentiation with respect to x . M_2 is the second moment of the transition kernel; the restriction on the $\omega(x,y)$, described above, implies⁸² that the kernel may be expanded in terms of its moments, and that the first moment, as well as the third and higher moments, may be discarded. The function $f(x)$ is the equilibrium (Boltzmann) distribution for the states as labeled by x .

If now we make the following formal analogies:⁸²

$$M_2 \equiv (\hbar^2/\mu); \quad \frac{1}{2}M_2[(\sqrt{f})'/\sqrt{f}] \equiv V(x); \quad +\lambda \equiv E \quad (98)$$

then eq 97 takes the form of a Schrodinger equation for a particle of mass μ in a one-dimensional potential $V(x)$. By inspection, $(\lambda_1 = 0, \psi_1 = \sqrt{f})$ is a solution, as required, and since $\lambda_1 = 0$ is known^{69,70} to be the smallest eigenvalue, this is the ground state of the quantum-mechanical analogue.

Further progress requires information about $V(x)$, as given by eq 98; bearing in mind that $\sqrt{f(x)}$ is proportional to $\exp[-U(x)/kT]$, $V(x)$ corresponding to Figure 1 will have the general form of Figure 2b. (It should be borne in mind that x is

interpreted as a position coordinate, and $V(x)$ as a potential function, only by analogy; in fact, x is a label to enumerate the states, and $V(x)$ is related to the equilibrium distribution function).

Since the ground-state wave function $\sqrt{f(x)}$ has substantial values in both A and B regions (i.e., the equilibrium constant is not too different from unity), the two wells must be in "resonance" in the sense long familiar in quantum chemistry. Had the $V(x)$ barrier in Figure 2 been infinitely high, the two $V(x)$ wells would have had coincident ground-state energies. However, the barrier is large but finite, so the two lowest eigenvalues $E_1 = \lambda_1 = 0$, and $E_2 = \lambda_2$, are nearly degenerate, while the gap corresponding to the next highest state is much larger than the gap separating E_1 and E_2 .

If Figures 1 and 2 had contained m potential wells, corresponding to m chemical species, similar conclusions would have applied;⁸³ now, however, a multidimensional Schrodinger equation analogue must be used. Once again, there are m nearly degenerate eigenvalues, including $\lambda_1 = 0$, arising from the resonance of m wells, while the gap between λ_m and λ_{m+1} is much larger than any of the $(m - 1)$ gaps separating the first m eigenvalues. The connection between the eigenvalue spectrum (eq 87 and eq 95) and the number of chemical species is now clarified.^{82,83}

Unfortunately, the fashion in which detailed balance arises from this same treatment is not susceptible to as simple an explanation as is the nature of the eigenvalue spectrum (for details see Appendix B). Consideration of the wave functions $\psi(x)$ of the quantum-mechanical analogue leads to a crucial orthogonality condition,⁸³ which for simplicity is here written for the three-isomer case only:

$$\frac{u_2 u_3}{a^*} + \frac{v_2 v_3}{b^*} + \frac{z_2 z_3}{c^*} = 0 \quad (99)$$

where all of the symbols were defined for eq 96 above. Equation 99 is an approximate relation, arising from the known orthogonality of the wave functions of the quantum-mechanical analogue,⁸³ which in turn may be traced ultimately to microscopic reversibility in the kinetic formulation; in addition, as stressed in the derivation in Appendix B, eq 99 also contains chemical information, external to, but consistent with, the physical description afforded by the master equation. This involves a classification, of the states labeled by the index i into chemical species, which in accord with chemical intuition involves placing the interspecies boundaries in regions of high potential energy. It is interesting to note that, formally, the local equilibrium approximation is *not* limited in this way; *any* assignment of the states to "chemical species" could be made, giving K_E constructs as in eq 86, which necessarily obey detailed balance as a direct consequence of microscopic reversibility.

However, the generalized eigenvalue approximation now involves both eq 87 (eigenvalue spectrum) and eq 99 (orthogonality condition) and is valid *only* for a chemically reasonable assignment of the states; the formulas⁸³ for the rate constants k_{AB}^λ , etc., are given in Appendix B as eq B21, and these obey detailed balance. For a two-species case, the orthogonality condition eq 99 is an *exact* consequence of the conservation of mass, so that, in accordance with the discussion of section II.B, detailed balance is a purely macroscopic requirement in such a case (see Appendix B).

It seems worthwhile, at this point, to recapitulate the main features of the foregoing discussion. It is possible to devise a physical model, couched in the language of linear algebra, corresponding to a chemical isomerization reaction. It is possible to derive an exact solution to this model (eq 77), which is not, without further approximations, consistent with the phenomenological rate equations of chemical kinetics. Two such rival approximations are considered; the local equilibrium ap-

proximation is the more traditional view, and invariably yields detailed balance as a direct consequence of microscopic reversibility.^{3,62} The eigenvalue approximation, when fully evaluated,^{82,83} also yields detailed balance, even for the crucial case of closed-loop mechanisms. In the special two-isomer case, the eigenvalue approximation may be shown to be a steady-state approximation of a special type (eq 90), and to contain the local equilibrium assumption as a limiting case.⁷¹

It can be shown that, in *general*, the eigenvalue approximation is less restrictive (i.e., it is valid over a wider range of conditions) than is its local equilibrium counterpart.^{77,85} The ultimate test of any theory must involve a comparison of its predictions with experimental observation; some small effort in this direction is attempted in section IV. However, it is possible, within the limits of the present theoretical framework, to show that the eigenvalue approximation is less restrictive.^{77,85} The raw experimental observations to be accounted for constitute measurements of the chemical composition as a function of time; the "exact" theoretical constructs, corresponding to the macroscopic composition variables, are given for the three isomer case by substituting eq 77 into eq 93. These expressions are "exact" in the sense that the only assumptions involved are those inherent in the master equation (eq 76) and in the chemical classification (eq 93). Predictions of the composition can be constructed⁷⁷ corresponding to each of the two rival approximations. Since all three expressions have the same equilibrium ($t \rightarrow \infty$) limiting values, the differences between them must be diminishing functions of time; it is possible to show⁷⁷ that the eigenvalue approximation to the composition approaches the "exact" prediction, to within some factor related to experimental uncertainty, faster than does the local-equilibrium approximation. Thus, although the orthogonality relation (eq 99) was derived⁸³ in a very approximate fashion, it does, when included as an integral feature of the eigenvalue approximation, yield the least restrictive known solution to the kinetic problem.^{77,85}

5. Limitations of Present Treatment

A limiting assumption, implicit in the entire treatment thus far (including section II), has been the restriction to systems in which the chemical reaction mechanism has been permitted to evolve spontaneously with time to the equilibrium state. Such systems are indeed a major concern for chemical kinetics; however, some of the major advances in chemical kinetics have come from well-designed experiments in which just one of the elementary mechanistic steps has been isolated for study, often in isolation even from its own "reverse" reaction. In such cases, the question of detailed balance requires some additional comment.⁷⁷

The question of a chemical principle of detailed balance can clearly arise only for elementary reactions which are reversible in the colloquial sense described above. On the other hand, "isolation" experiments of the type referred to usually arrange artificial conditions so that the reaction becomes effectively irreversible in the colloquial sense; trapping experiments are typical, and an example will be considered in section IV below. If it is possible to separately study both "directions" of an elementary reaction in this fashion, the discussion so far has little to say concerning the applicability of detailed balance to the rate coefficients thus measured; *only* if the local equilibrium approximation is valid does detailed balance *necessarily* apply in such cases,⁷⁷ while the eigenvalue approximation may or may not be consistent with such a circumstance. Observations of the breakdown of detailed balance are thus evidence for the inapplicability of the local equilibrium approximation, and examples of such behavior are discussed below.

Another serious restriction on section III is its limitation to ideal gas systems; while this permitted the use of single-molecule state functions in the theoretical discussion, a major portion of

interesting chemistry is thereby excluded. The work of Golden^{37,56} has already been mentioned in this regard; unfortunately, this approach involves a specialized mathematical background not normally included in the training of the vast majority of practicing chemists. To summarize briefly, Golden has found it possible to develop a formalism suitable for imposing chemical restrictions upon the general physical description of a system of fundamental particles not necessarily forming an ideal gas. The time variation of such a restricted theoretical model can be expressed in a form which formally matches the description afforded by phenomenological chemical kinetics, although there appears to be a certain residual ambiguity in the quantities which may be identified as the rate constants.^{37,56} Nonetheless, principles corresponding to the present microscopic reversibility and detailed balance may be derived regardless of these ambiguities, as a result of constraints which correspond to what have here been termed time-reversal-symmetry and the portability of rate constants.

An excellent example of the difficulties involved in extracting chemistry from formally complete physical theories of time-dependent phenomena^{37,56} is offered by the work of Thomsen⁸⁶ and of Landsberg.^{87,88} The logical connections between quantum-statistical principles, such as microscopic reversibility, and macroscopic laws, such as the increase of entropy in isolated systems, may be clearly demonstrated. Such connections must, of course, exist if current quantum-statistical theories really are to account for all observed regularities in nature; thus, the distinction drawn here between "microscopic" and "macroscopic" restrictions on chemical kinetics would possibly be better rephrased as "theoretical" and "phenomenological" restrictions. However, these rather elegant and logically complete descriptions⁸⁶⁻⁸⁸ of the formal relationships between some fundamental principles are useless in all but a general pedagogic sense for the present *chemical* discussion. The states considered⁸⁶⁻⁸⁸ are complete system states, with absolutely no chemical information in the description.

6. Transition State Theory

This is clearly the theory of chemical kinetics most widely used by practising chemists. Its origins may be traced back to the work of Arrhenius,⁸⁹ and it was put on a quantitative predictive basis chiefly through the work of Wigner, Pelzer, Polanyi, Evans, and Eyring (see ref 60); more modern versions, particularly the bond-energy-bond-order method due to Johnston,⁸⁴ can be remarkably successful in light of the approximations and conceptual difficulties of the theory.^{84,90} It seems appropriate to indicate briefly how the present work relates to this theory; it is clear, from the outset, that it is a "local equilibrium" theory.

As a quantitative predictive theory, transition state theory applies only to elementary reactions in ideal gas systems; in addition, as will be explained further below, the early formulations are most readily applied to irreversible reactions, in the colloquial sense. Then, the theory applied to the $A \rightarrow B$ isomerization would assume that the "activated complex", situated at the energy maximum in Figure 1, is in equilibrium with the reactant A; the internal states are further classified into rotational, vibrational, and electronic states, in the usual way. Further, it is assumed that a normal-mode vibrational analysis may be applied to the activated complex, and that just one of these modes, the "reaction coordinate", may be identified as the "progress variable" for the reaction, e.g., the twisting angle of an olefin; *only* motions along this single reaction coordinate are assumed to lead to chemical reaction. Then, the rate of $A \rightarrow B$ transformations is assumed to be given by:

$$\begin{aligned} \text{rate of } A \rightarrow B &= \nu(\text{concn of activated complex}) \\ &= \nu K_c(\text{concn of reactant}) = \nu q_R K_c^\ddagger(\text{concn of reactant}) \quad (100) \end{aligned}$$

where ν is the frequency for motion along the reaction coordinate at the energy maximum, q_R is the molecular partition function for this coordinate, and K_c is the equilibrium constant in concentration units (i.e., for a standard state of unit concentration) for the reactant-activated complex equilibrium; K_c^\ddagger is simply (K_c/q_R) . Then, if q_R is treated as a vibrational partition function for frequency ν such that $kT \gg h\nu$, eq 100 reduces to the well-known form:

$$k_{AB} = (kT/h)K_c^\ddagger \quad (101)$$

where K_c^\ddagger is, in principle, evaluable from a guess as to the detailed structure of the activated complex. Now, an additional correction is applied to eq 101; it was assumed above that the division between reactant and product fell at the maximum in Figure 1. However, systems are normally only detected experimentally as having been transformed to product B if they reach the foot of the potential well assigned to B (Figure 1). The ubiquitous "transmission coefficient" κ is supposed to account for cases where a crossing of the boundary at the potential energy maximum does not yield a B molecule deep in the potential well, but involves a trajectory whereby the system returns to the A well. That is, there are two boundaries considered: that at the energy maximum in Figure 1, corresponding to the activated complex, and another somewhere close to the potential minimum labeled B. The primary theory deals with the former boundary, and the transmission coefficient accounts for that fraction of the trajectories which succeed in crossing *both* boundaries. Thus, eq 101 becomes:

$$k_{AB} = \kappa(kT/h)K_c^\ddagger \quad (102)$$

Unfortunately, in practice κ has tended to become "... a parameter that adjusts a theoretically derived rate constant to the observed value".⁹¹ However, a more qualitative problem arises when the theory sketched in above is considered in terms of detailed balance.

If the $B \rightarrow A$ reaction is treated in an analogous fashion, the rate constant k_{BA} may be derived as:

$$k_{BA} = \kappa'(kT/h)(K_c^\ddagger)' \quad (103)$$

Equations 102 and 103 are the transition state theory expressions for k_{AB} and k_{BA} , obtained by considering each of the $A \rightarrow B$ and $B \rightarrow A$ reactions, in turn, as irreversible reactions; that is, in both cases, recrossings of the boundary at the energy maximum were counted in κ or κ' , *not* in the appropriate reverse reaction rate constant. Then, if the two rate constants were actually measured under irreversible conditions, in the colloquial chemistry sense, e.g., by suitable trapping experiments, the local-equilibrium property is *not* now sufficient to guarantee detailed balance since, in addition, the relation $\kappa = \kappa'$ must be satisfied.⁹² The transmission coefficients depend upon the topology of the complete potential surface, the latter usually being different for the two sides of the activated complex; it is also difficult to conceive how κ and κ' could remain constant for different temperatures. Thus, for rate constants measured in artificially constrained irreversible systems, transition-state theory does *not* necessarily require detailed balance, even although it is a local equilibrium theory.

For reactions carried out under reversible conditions, again in the colloquial sense, the theory as outlined above is useless as a rate theory; this is basically because, if the activated complex is at equilibrium with *both* reactants and products, then reactants and products must be in equilibrium with one another. The theory must now be reformulated,² but to do so successfully, a *single* boundary separating reactants for products must be accepted; that is to say, any trajectory which recrosses this boundary is to be counted *not* as a contribution to κ , but as a forward reaction followed by a reverse reaction.

A distinction is now drawn between those activated com-

plexes moving along the reaction coordinate in the $A \rightarrow B$ direction, and those with a reverse direction of motion in this mode; the former are assumed to be in equilibrium with A, and the latter with B. Then, eq 102 and eq 103 become:

$$k'_{AB} = v^{\rightarrow} \times q_{R^{\rightarrow}} \times K_c^{\ddagger} = \frac{1}{2}(kT/h)(K_c^{\ddagger}) \quad (104)$$

$$k'_{BA} = v^{\leftarrow} \times q_{R^{\leftarrow}} \times (K_c^{\ddagger})' = \frac{1}{2}(kT/h)(K_c^{\ddagger})' \quad (105)$$

Here, $v^{\rightarrow} = v = v^{\leftarrow}$ are the frequencies of motion in the two directions, and $q_{R^{\rightarrow}}$ and $q_{R^{\leftarrow}}$ are the partition functions for the reaction coordinate in the two directions; it is assumed $q_{R^{\rightarrow}} = \frac{1}{2}q_R = q_{R^{\leftarrow}}$, so that the transmission coefficients relevant to the irreversible case have been replaced by an assumption concerning the motional symmetry of the reaction coordinate partition function (i.e., no anharmonicity). This formulation² removes the problem associated with complete equilibrium and also permits detailed balance to be obeyed; the latter is here a purely macroscopic requirement, as discussed in section II.

When applied to reactions in other than ideal gas systems, transition state theory usually loses its quantitative pretensions and becomes a useful language in which to express experimental results; the crucial additional assumption, which permits even this, concerns the direct dependence of the rate on the concentration of the activated complex, and *not* on its thermodynamic activity. The well-known dependence of the rate of ionic reactions in solution on the reactant charges and the ionic strength necessitates this assumption; the same assumption has been tested for reactions in nonideal gases⁹³⁻⁹⁵ and found to be valid. Thus, for the simple reversible isomerization reaction in solution, transition state theory gives the following expression for the rate:

$$-d(A)/dt = k'_{AB}(\gamma_A/\gamma_{\ddagger}^{\rightarrow})(A) - k'_{BA}(\gamma_B/\gamma_{\ddagger}^{\leftarrow})(B) \quad (106)$$

where k'_{AB} and k'_{BA} are the ideal gas rate constants given by eq 104 and eq 105, provided that the γ 's are fugacity coefficients measured relative to the ideal gas as standard state; comparison with eq 19 permits the identification $\beta = (\gamma_{\ddagger}^{\rightarrow})^{-1}$ and $\beta' = (\gamma_{\ddagger}^{\leftarrow})^{-1}$. The empirical finding that $\beta = \beta'$ is now understandable in terms of transition state theory, since the nonideal interactions of the activated complex are unlikely to depend upon the instantaneous direction of motion along the reaction coordinate. Further, the rate as given by eq 106 is entirely consistent with the thermodynamic restrictions described in section II. In the event that thermodynamic activities, measured relative to some standard state other than the ideal gas state, are used in eq 108, multiplication of each of the two terms in eq 108 by a dimensionless constant would be necessary, thus preserving the detailed balance relationship. Extension of these ideas to chemical mechanisms with closed loops is obvious, so that the discussion for ideal gases may be transferred directly to solution reactions, within the limitations of transition state theory. This is basically possible because the theory, as applied to solution reactions, very neatly avoids the worst problems of chemical classifications^{37,56} by adopting ideal gas theories plus a purely operational definition of chemical composition in solution, as used to define thermodynamic activities and fugacities.

IV. Practical Applications

A. General Remarks

The relationships described in section II above have become so well established in chemical practice that any deviations from them seem suspect. Nonetheless, examples of such deviations are known, and most of the discussion below will be devoted to such cases; as shown above, particularly in section III.C.5, detailed balance is not an ironclad requirement for all experiments in chemical kinetics. Application of such relationships is usually valid, but caution is necessary to ensure that exceptional circumstances do not preclude their applicability. Many examples

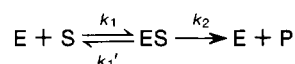
could be drawn from the literature which satisfy the relationships of section II in a self-consistent manner; the examples actually chosen were deemed to be particularly well established or to exemplify some additional feature not covered in the above discussion.

B. The Hydrogen-Iodine-Hydrogen Iodide System

This gas-phase reaction system is probably the most thoroughly investigated kinetic mechanism in the literature. Sullivan,⁹⁶ who was responsible for this elegant work, has reviewed the experimental data from the point of view of the present discussion and found the appropriate detailed balance relationship to be well satisfied for the reversible elementary reaction $H_2 + 2I \rightleftharpoons 2HI$. Sullivan's analysis⁹⁶ was restricted to temperatures where this was the only elementary process occurring (apart from the equilibration $2I + M \rightleftharpoons I_2 + M$). However, extraction of detailed balance was *not* a relatively trivial macroscopic requirement (section II) in this case, since the two rate constants involved were obtained under rather different experimental conditions, in one case involving photochemistry. Thus, the observed validity of detailed balance would seem to imply, in view of the considerations of section III.C.5 above, that microscopic reversibility must be invoked and that the local equilibrium interpretation of the observed rate constants is adequate in the present case, insofar as presently available information is concerned. Thus, Sullivan⁹⁶ did, in fact, show that the possible participation of electronically excited I_2 in the reaction was consistent with the observed detailed balance provided that the relevant local equilibrium was indeed established. It might be added here that Sullivan's interpretation of his experimental data is not entirely without difficulties; in particular, some reservations exist with respect to his claim that, at lower temperatures, the thermal reaction between H_2 and I_2 proceeds *not* via a mechanism involving a bimolecular, four-center collision, but instead involves the interaction of H_2 with two iodine atoms. Recently, Raff et al.¹²⁰ performed semiempirical calculations of the H_2I_2 interaction potentials and investigated the dynamics of the hydrogen-iodine reaction by classical trajectory calculations.¹²¹ This work supported the claim⁹⁶ that the four-center molecular mechanism is forbidden, but required an attractive well for the H_2I complex of about $1.65 \text{ kcal mol}^{-1}$. Very recent experimental values¹²² for this well depth are about five times smaller than this, thus casting doubt upon the theoretical conclusions. In addition, it is at least possible¹²³ that Sullivan's original experimental data do not preclude a mechanism whereby the reaction proceeds via a four-center collision between H_2 and an I_2 molecule possessed of considerable vibrational and rotational excitation; the latter species would be in a steady state, or quasi-equilibrium of some kind, with respect to iodine atoms, thus making it very difficult to distinguish between the two mechanisms. However this question is finally resolved, it appears unlikely that the conclusions, pertinent to the present question of detailed balance, will be affected.

C. Enzyme Kinetics: the Haldane Relationships

The basic mechanism proposed for enzyme reactions is known as the Michaelis-Menten mechanism;⁹⁷ in its various modifications it is still widely used as a convenient framework in which to report experimental data, although the actual mechanisms of enzyme reactions are known to be much more complex than implied by the original simple idea.⁹⁷ For an irreversible enzyme reaction (in the colloquial sense), the mechanism may be simply written as:

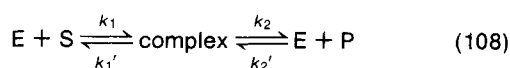


Originally,⁹⁷ it was proposed that the enzyme E and substrate S were in equilibrium with the complex ES; however, the conventional steady-state assumption has been applied⁹⁸ to the ES concentration. The observed expression for the rate is:

$$\frac{d(P)}{dt} = \frac{k_2(E)_0(S)}{K_m + (S)} = \frac{V_{\max}(S)}{K_m + (S)} \quad (107)$$

Equation 107 gives the correct functional form for the observed gross rates of many irreversible enzyme reactions; $(E)_0 = (E) + (ES)$ is constant. In the steady-state interpretation,⁹⁸ the Michaelis constant K_m is given by $(k_1' + k_2)/k_1$, while in the local equilibrium limit,⁹⁷ $k_2 \ll k_1'$, and K_m is the dissociation constant for ES. The saturation behavior typical of such reactions (when $(ES) = (E_0)$), is made explicit by the second form of writing eq 107, where $V_{\max} = k_2(E_0)$ is the limiting rate; clearly, K_m is equal to the value of (S) which gives a rate equal to $0.5 V_{\max}$.

Considerations such as those discussed here apply to a reversible enzyme reaction, e.g.,



Application of the steady-state treatment to eq 108 gives the following rate expression:

$$d(P)/dt = [(V_f/K_f)(S)] / [1 + (S)/K_f + (P)/K_r] \quad (109)$$

where $V_f = k_2(E_0)$, $V_r = k_1'(E_0)$, $K_f = (k_1' + k_2)/k_1$, and $K_r = (k_1' + k_2)/k_2'$. Again, many reversible enzyme reactions are found to follow a rate expression of this general form.

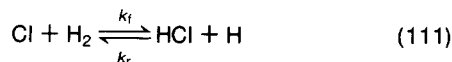
The Haldane relationship⁹⁹ arises from requiring that the rate described by eq 109 shall vanish if, and only if, the concentrations are such as to satisfy the thermodynamic equilibrium conditions; thus, it is a special case of the considerations of section II above. Ignoring nonideal effects, as was done for the rate expressions eq 107 and eq 109, so that $[(P)/(S)]_{\text{eq}} = K_c$, it is clear that the corresponding restriction on the kinetic parameters is:⁹⁹

$$(V_f K_r / V_r K_f) = K_c \quad (110)$$

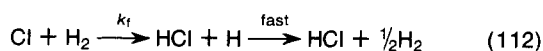
It is trivial to rewrite the above derivation of the Haldane relationship (eq 110) in terms of thermodynamic activities instead of concentrations. More complex mechanisms than that given by eq 108 have been treated in an analogous fashion,¹⁰⁰⁻¹⁰² yielding relationships similar to eq 110 as a consequence of requiring that the equilibrium state be independent of the language (kinetic or thermodynamic) used to describe it.

D. The System: $\text{Cl} + \text{H}_2 \rightleftharpoons \text{HCl} + \text{H}$

By using electron spin resonance to follow the free atom concentrations, Westenberg and de Haas¹⁰³ studied the gas-phase reaction system:

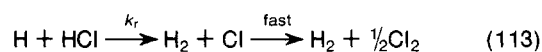


The rate constant k_f , for example, was measured by mixing a nonequilibrium concentration of Cl atoms in a very large excess of H_2 ; the decay of Cl atoms was found to follow pseudo-first-order kinetics. The chemical mechanism relevant to this experiment was thus:



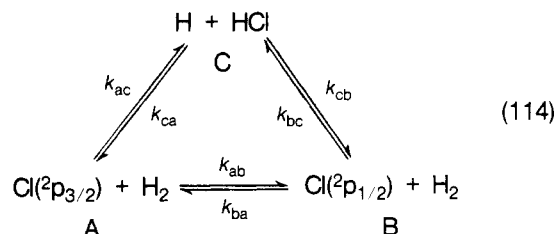
where the recombination of H atoms was much faster than the reverse reaction since $(\text{H}_2) \gg (\text{HCl})$; thus, the forward reaction was separated out from other mechanistic steps, and made "irreversible", by effectively trapping the product hydrogen atoms.

Similarly, the reverse reaction was studied¹⁰³ by mixing H atoms with a large excess of HCl:



The ratio (k_f/k_r) , thus experimentally measured over a range of temperature, was found to be smaller than the equilibrium constant K_e for the reaction given by eq 111, by a factor of 2 to 3, far outside experimental uncertainty. Clearly, a local-equilibrium interpretation of k_f and of k_r is unable to account even qualitatively for these observations; on the other hand, a satisfactory explanation based upon the nonequilibrium eigenvalue approximation has been given by Snider.¹⁰⁴ This will be reiterated here in some detail, as it provides an excellent and simple example of the somewhat abstract discussion in section III.C above.

The necessary first step is to identify the internal mode most likely to be in disequilibrium. The time scale of the chemistry was such¹⁰⁴ that all translational, rotational, and vibrational degrees of freedom must have been essentially equilibrated.⁷⁶ Excited electronic states of H_2 , HCl, and H were effectively unpopulated at the experimental temperatures; however, the $^2p_{1/2}$ state of Cl atoms is only some 2.5 kcal/mol⁻¹ above the $^2p_{3/2}$ ground state, and Snider's explanation¹⁰⁴ of the experimental observations¹⁰³ is based upon an assumed nonequilibrium of these two states due to the comparable rates of the chemical reaction and of the internal relaxation. (The idea¹⁰⁴ that the $^2p_{1/2}$ state may be much more reactive than the $^2p_{3/2}$ state appears to have been first suggested by Herzberg.¹⁰⁵) The relevant detailed scheme is:



Equation 114 is the simple, three-level physical model for the chemical reaction given by eq 111. In each of states A, B, and C, the diatomic gas is taken to be in large excess, so that the microscopic rate constants $[k_{ab}(\text{H}_2)]$, etc., are pseudo first order. However, in the experimental study of the forward reaction (eq 112), the concentration of HCl was so low that $[k_{ca}(\text{HCl})] \approx 0 \approx [k_{cb}(\text{HCl})]$; similarly, in the study of the reverse reaction, $[k_{ac}(\text{H}_2) \approx 0 \approx [k_{bc}(\text{H}_2)]$, due to the experimental arrangement.¹⁰³

First, the local-equilibrium approximations to the rate constants may be derived as follows:

$$\begin{aligned} -d(\text{Cl})/dt &= -(d/dt)[(^2p_{3/2}) + (^2p_{1/2})] = [k_{ac}(^2p_{3/2}) \\ &\quad + k_{bc}(^2p_{1/2})](\text{H}_2) \\ &= (\text{Cl})\{k_{ac}[(^2p_{3/2})/(\text{Cl})]_{\text{eq}} + k_{bc}[(^2p_{1/2})/(\text{Cl})]_{\text{eq}}\}(\text{H}_2) \\ &= (\text{Cl})\{k_{ac}[k_{ba}/(k_{ba} + k_{ab})] + k_{bc}[k_{ba} + k_{ab}]\}(\text{H}_2) \\ &= (\text{Cl})\{(k_{ac}k_{ba} + k_{bc}k_{ab})/(k_{ba} + k_{ab})\}(\text{H}_2) \\ &= (\text{Cl})(\text{H}_2)k_f^E \end{aligned} \quad (115)$$

The first line of eq 115 uses the fact that, for the experimental study of the forward reaction,¹⁰³ $k_{ca} = 0 = k_{cb}$. The second line introduces the local equilibrium approximation with respect to the electronic states of Cl; the expressions for the equilibrium fractions used in the third line are a consequence of microscopic reversibility, $k_{ab}(^2p_{3/2})_{\text{eq}} = k_{ba}(^2p_{1/2})_{\text{eq}}$. The rest of eq 115 is simply algebra.

The analogous treatment for the reverse reaction, as given by eq 113, with $k_{ac} = 0 = k_{bc}$, is:

$$-d(\text{H})/dt = (k_{ca} + k_{cb})(\text{H})(\text{HCl}) = k_r^E(\text{H})(\text{HCl}) \quad (116)$$

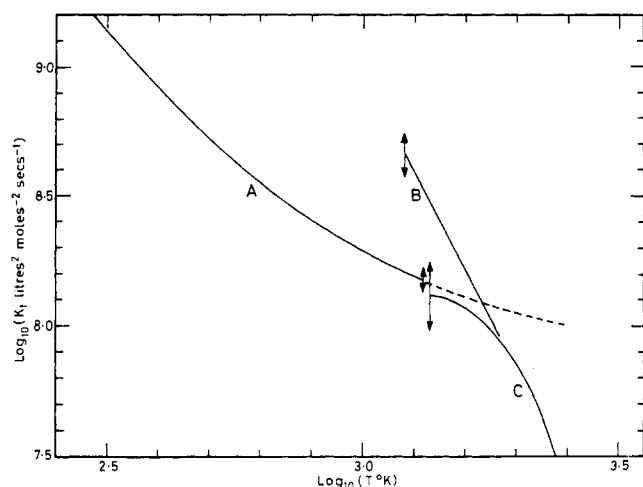
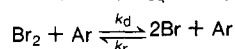


Figure 3. Early results for k_f or (k_d/K_{eq}) , for system



(A) Flash photolysis values for k_f (ref 108); (B) shock tube values for (k_d/K_{eq}) (ref 109); (C) shock tube values for (k_d/K_{eq}) (ref 110).

Use of microscopic reversibility, applied to k_{ab} , etc., plus some algebraic manipulation then leads to the following relation:

$$\begin{aligned} K_e &= \{(\text{H})(\text{HCl})/(\text{H}_2)[(^2p_{3/2}) + (^2p_{1/2})]\}_{eq} \\ &= k_{ab}k_{bc}/k_{cb}(k_{ba} + k_{ab}) \\ &= (k_{ab}k_{bc} + k_{ac}k_{ba})/[(k_{ba} + k_{ab})(k_{ca} + k_{cb})] \\ &= k_f^E/k_r^E \end{aligned} \quad (117)$$

(The third line of eq 117 corresponds to eq 2c of Snider's original paper;¹⁰⁴ in the latter, a misprint has replaced k_{ca} in the denominator by k_{ac}). As expected from the discussion of section III.C above, the local equilibrium approximation predicts that detailed balance should be obeyed, and is thus in disagreement with observation.¹⁰³

If now the corresponding eigenvalue approximations are constructed, the treatment of the reverse reaction experiment (eq 113) is unchanged, so that:

$$k_r^\lambda = k_r^E = (k_{ca} + k_{cb})(\text{HCl}) \quad (118)$$

For the forward reaction (eq 112), however, the appropriate master equation (cf. eq 76) is:

$$\begin{aligned} \left[\frac{1}{(\text{H}_2)} \right] \left(\frac{d}{dt} \right) \begin{pmatrix} (^2p_{3/2}) \\ (^2p_{1/2}) \\ (\text{HCl}) \end{pmatrix} \\ = - \begin{pmatrix} (k_{ab} + k_{ac}) & -k_{ba} & 0 \\ -k_{ab} & (k_{ba} + k_{bc}) & 0 \\ -k_{ac} & -k_{bc} & 0 \end{pmatrix} \begin{pmatrix} (^2p_{3/2}) \\ (^2p_{1/2}) \\ (\text{HCl}) \end{pmatrix} \end{aligned} \quad (119)$$

The zeroes in the last column reflect the experimentally arranged condition $k_{ca}(\text{HCl}) \approx 0 \approx k_{cb}(\text{HCl})$. The transport matrix has $\lambda_1 = 0$, as required, and the other eigenvalues are the roots of the characteristic equation:

$$\lambda^2 - \lambda(k_{ab} + k_{ba} + k_{ac} + k_{ca}) + (k_{ab}k_{bc} + k_{ac}k_{cb} + k_{ac}k_{ba}) = 0 \quad (120)$$

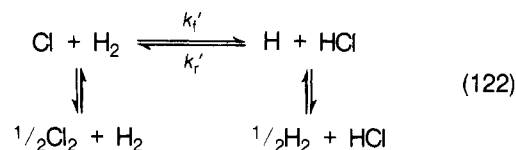
It is, of course, possible to solve eq 120 exactly for λ_2 and λ_3 ; however, if the eigenvalue approximation $\lambda_2 \ll \lambda_3$ is valid, for this two "species" case (eq 112), a good approximation to λ_2 is:

$$\lambda_2 \approx \lambda_2\lambda_3/(\lambda_2 + \lambda_3) = (k_{ab}k_{bc} + k_{ac}k_{cb}) / (k_{ab} + k_{ba} + k_{ac} + k_{bc}) = k_f^\lambda(\text{H}_2) \quad (121)$$

The identification of λ_2 with $k_f^\lambda(\text{H}_2)$ arises from eq 87, since in the experiment (eq 112) to which eq 119 applies, k_r^λ was arranged to be zero. The condition $\lambda_2 \ll \lambda_3$ must, in the light of Widom's analysis^{82,83} (see Appendix B), correspond to the feasibility of accepting the $^2p_{3/2}$ and $^2p_{1/2}$ states as representing internal states of a single recognizably chemical species Cl, rather than as two distinct chemical species. In the present case, this requires that the energy separation of the two states (2.5 kcal mol⁻¹) be much smaller than the energy barrier separating (Cl + H₂) from (H + HCl); unfortunately, the observed¹⁰³ activation energy for k_f (4.3 kcal mol⁻¹) is not readily interpreted in terms of the height of an activation barrier (cf. Figure 1), since the expression for k_f^λ (eq 121) is a complex function of four rate constants. Indeed, if eq 118 and eq 121 do in truth provide the correct interpretation of the experimental observations, it is a matter for surprise that the Arrhenius plots for k_f and k_r gave such excellent straight lines.¹⁰³

It is clear that $k_f^\lambda/k_r^\lambda \neq K_e$; by making reasonable guesses at numerical values for ratios of detailed rate constants, Snider¹⁰⁴ was able to reproduce the observed¹⁰³ behavior of $[(k_f/k_r)/K_e]$ fairly closely. Thus, in this case, the eigenvalue approximation¹⁰⁴ can offer an excellent account of the experimental observations,¹⁰³ with some minor reservations concerning the *separate* temperature dependences of k_f and of k_r ; the local equilibrium approximation, on the other hand, fails totally.

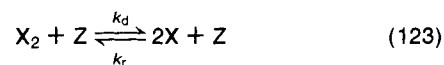
The only remaining quibble⁷⁷ concerns the designation of the measured¹⁰³ parameters k_f and k_r as rate constants; while these were clearly independent of time, they cannot be independent of the initial conditions of the experiment; i.e., they are not portable. For example, had the experimental conditions been such as to permit (H₂) \approx (HCl) and (H) \approx (Cl), the following chemical mechanism would have to be considered:



Since eq 122 is a chemical mechanism with no closed loops, the detailed balance relationship $(k_f'/k_r') = K_e$ is a purely macroscopic requirement (section II); thus either $k_f' \neq k_f$, or $k_r' \neq k_r$, or both. The relevant master equation would be the same as eq 119, except that the final column of the transport matrix would have the zeroes replaced by the appropriate combinations of k_{ca} and k_{cb} . It is clear, without deploying all the algebra, that both rate constants must, in fact, change. As a possibly pedantic conclusion, it would seem more consistent to refer to the measured¹⁰³ k_f and k_r as "rate coefficients".

E. Dissociation-Recombination Reactions of Homonuclear Diatomic Molecules

The reactions to be discussed here are of the type:



where X is an atom, and Z is an inert gas, typically argon. The question of detailed balance for such reactions has been discussed at some length by Rice¹⁰⁶ and Pritchard;¹⁰⁷ it is probably fair to say that this discussion has now been out-dated by subsequent experimental and theoretical findings, to which these authors^{106,107} have themselves significantly contributed.

The experimental data in question are exemplified by the sketch in Figure 3; for the example most extensively investigated, bromine in argon,¹⁰⁸⁻¹¹⁰ the correct diagram corresponding to Figure 3, with an indication of the experimental precision, is available.¹¹¹ The points to be noted are: (a) The flash photolysis results of k_r , at the highest temperatures, had to be

corrected¹⁰⁸ for redissociation on the basis of $(k_d/k_r) = K_e$, in accordance with the principles of section II above. (b) The shock tube data^{109,110} transformed by use of the detailed balance relation, disagree significantly with one another at their low-temperature limit. The data obtained¹¹⁰ by following the first atom concentration behind the shock front agree with the flash photolysis data¹⁰⁸ at the overlap temperature (about 1300 K for bromine in argon). (c) The temperature dependences of the three sets of data all disagree.

Again, the observed deviations from detailed balance, if real, must correspond to a breakdown of the local equilibrium approximation. An approximate nonequilibrium model, related to the eigenvalue approximation, was designed^{111,112} to reconcile the discrepancies apparent in Figure 3 in terms of only measurable physical parameters. Apart from the approximations inherent in this theory,^{111,112} one crucial parameter (the vibrational relaxation time of Br₂ in argon) had to be estimated, as it has not been measured over the relevant temperature range.

More recently, however,^{113,114} a critical reevaluation of the experimental techniques used, together with the additional use of the laser-schlieren technique as an independent experimental method, has shown that the atomic emission method (curve III of Figure 3) is unreliable at higher temperatures. These most recent findings^{113,114} indicate that all four experimental methods give results entirely consistent with one another via the detailed balance relationship, with the single exception of the early shock-tube data obtained using molecular absorption spectrophotometry, at the low-temperature limit of the technique (curve II, Figure 3). These findings throw doubt on the previous approximate model,^{111,112} or at least on its quantitative evaluation in the bromine-argon case. (The same model is rather successful¹¹¹ in accounting for certain features of the oxygen-argon system, for example.) The sole remaining discrepancy, that of molecular absorption spectrophotometry at low shock temperatures, is probably due to a systematic error of some kind in the shock tube experiments; it does not, however, appear to be explicable in terms of the best modern theories of nonideal shock tube behavior.^{109,110}

It seems relevant here to mention the recent work of Pritchard and his collaborators,¹¹⁵ who have been able to develop very efficient computer techniques permitting "numerical experiments" on the dissociation-recombination reactions of hydrogen in helium, in terms of the general framework discussed in section III. This work¹¹⁵ was not primarily directed toward investigating detailed balance, although the results are clearly of interest in this regard; under the conditions studied,¹¹⁵ detailed balance was well obeyed.

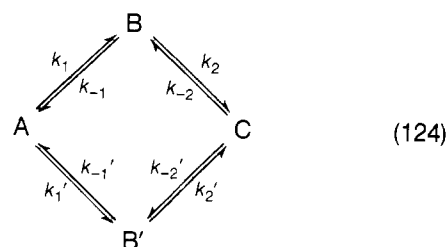
F. Implications for Complex Reaction Mechanisms

The present work has concentrated on certain quantitative relationships between kinetic and thermodynamic parameters. However, the same considerations of detailed balance are often used as a justification for the qualitative claim that the favored "kinetic pathway" for a reaction proceeding in one direction must be the same as that for the reverse reaction. For the trivial case of systems at complete equilibrium, all the considerations of sections II and III above would suggest that this claim must be valid, although it is, of course, not possible to test it experimentally.

However, the interpretation of the above claim is not usually concerned with equilibrium systems; rather is it applied to cases where artificial constraints are applied to the system, so that the overall reaction becomes effectively irreversible (in the colloquial sense), first in one direction and then in the other. As was seen in the simple example discussed in section IV.D, such procedures are not without their perils. An informative discussion of the mechanistic implications of the principle of detailed balance has been given by Krupka, Kaplan, and Laidler;¹¹⁶ the

following is an abbreviated version of their work, with some additional comments relevant to the present review.

The first simple example concerns the first-order network:



Species B and B' are supposed to be unstable intermediates, to which the usual steady-state approximation may be applied. Then, the rate is given, to within this approximation, by:

$$-\frac{d(A)}{dt} = \frac{d(C)}{dt} = \left[\left(\frac{k_1 k_2}{k_{-1} + k_2} \right) + \left(\frac{k_1' k_2'}{k_{-1}' + k_2'} \right) \right] \quad (A)$$

$$- \left[\left(\frac{k_{-1} k_{-2}}{k_{-1} + k_2} \right) + \left(\frac{k_{-1}' k_{-2}'}{k_{-1}' + k_2'} \right) \right] \quad (C) \quad (125)$$

Now suppose that:

$$\left(\frac{k_1 k_2}{k_{-1} + k_2} \right) = x \left(\frac{k_1' k_2'}{k_{-1}' + k_2'} \right);$$

$$\left(\frac{k_{-1} k_{-2}}{k_{-1} + k_2} \right) = y \left(\frac{k_{-1}' k_{-2}'}{k_{-1}' + k_2'} \right) \quad (126)$$

which may be combined to give:

$$\left(\frac{k_1 k_2}{k_{-1} k_{-2}} \right) = \left(\frac{x}{y} \right) \left(\frac{k_1' k_2'}{k_{-1}' k_{-2}'} \right) \quad (127)$$

However, as a consequence of detailed balance:

$$\left(\frac{k_1 k_2}{k_{-1} k_{-2}} \right) = \left[\frac{(B)(C)}{(A)(B)} \right]_{eq} = K_e$$

$$= \left[\frac{(B')(C)}{(A)(B')} \right]_{eq} = \left(\frac{k_1' k_2'}{k_{-1}' k_{-2}'} \right) \quad (128)$$

Clearly, eq 127 and eq 128 together yield the result $x = y$; this simple mathematical result seems quite unambiguous, within the stated assumptions.

However, what is not so clear is the verbal interpretation placed upon this result. The original authors¹¹⁶ interpreted $(k_1 k_2 / (k_{-1} + k_2))(A)$, for example, as the forward rate $A \rightarrow C$ via intermediate B, and $(k_{-1}' k_{-2}' / (k_{-1}' + k_2'))(C)$ as the reverse rate $C \rightarrow A$ via intermediate B', etc. If the elementary *chemical* rate constants k_1, k_1' , etc., are adequately represented by the local equilibrium approximation, then this "flux" interpretation is valid; however, if the eigenvalue approximation is necessary, no such interpretation is permissible, as emphasized by Widom.⁷² That these authors¹¹⁶ did indeed view the elementary rate constants as local-equilibrium fluxes is clear from the second paragraph of their paper,¹¹⁶ which is written very much in the spirit of the transition state theory. (Note that B and B' are *not* proposed activated complexes, but recognizable, albeit relatively unstable, chemical species; each of the rate constants k_1, k_2 , etc., is thus an elementary rate constant, to which the transition state theory is applicable.)

Thus, if the explicit assumption is made that the local equilibrium flux interpretation is indeed valid, each of the terms in eq 125 may be viewed as follows:

$$\left(\frac{k_1 k_2}{k_{-1} + k_2} \right) (A) = [k_1(A)] [k_2 / (k_{-1} + k_2)]$$

$$= [\text{rate of production of B from A}]$$

$$\times [\text{fraction of B which proceeds to C}] \quad (129)$$

Analogous interpretations may be written for the other terms of eq 125. Then, under the local equilibrium assumption applied

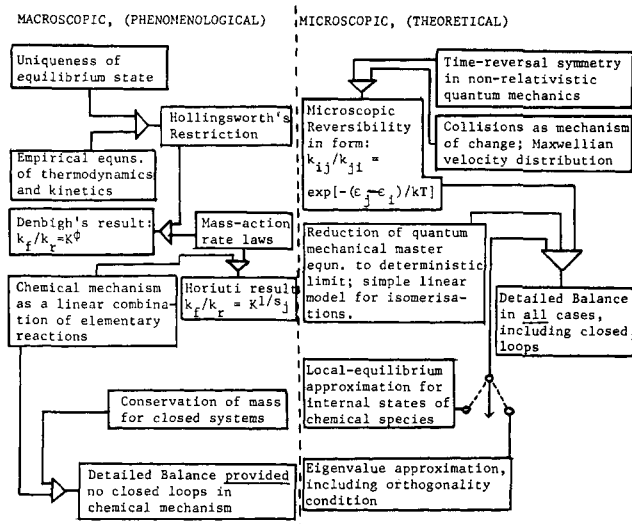
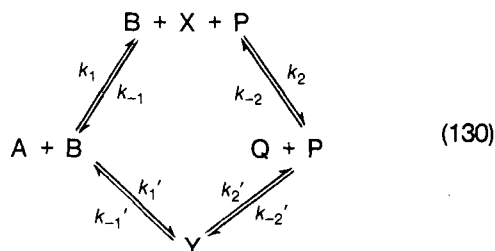


Figure 4. Diagrammatic summary of present work.

to the internal modes of each of the chemical species A, B, B', and C, eq 125–128 imply that each path, i.e., via B or B', is favored to the same extent in the two directions.¹¹⁶

This latter conclusion is not, however, valid for all kinetic schemes even within the local-equilibrium flux assumption. (This assumption here refers to the internal modes of each chemical species, *not* to equilibration of some of these species among themselves; with regard to the latter, only a steady-state assumption is necessary.) It turns out¹¹⁶ that the conclusion is invalid if all paths are not kinetically equivalent, in the sense that the reaction steps in the different paths are of different kinetic orders. A simple example of this situation is:¹¹⁶



If again the steady-state assumption is applied to the species X and Y, and the local equilibrium assumption applied to the internal modes of all species thus permitting the flux interpretation,⁷² the following relationships may be derived:¹¹⁶

$$\frac{v_f}{v_r'} = \frac{k_1 k_2 (k_{-1}' + k_2')}{k_1' k_2' [k_{-1}(P)_f + k_2(B)_f]} \quad (131)$$

$$\frac{v_r}{v_r'} = \frac{k_{-1} k_{-2} (k_{-1}' + k_2')}{k_{-1}' k_{-2}' [k_{-1}(P)_r + k_2(B)_r]} \quad (132)$$

v_f and v_r' are the forward rates via X and Y, respectively, and v_r and v_r' are the corresponding reverse rates; $(P)_f$ and $(B)_f$ are the concentrations in an experiment designed to study the forward reaction, while $(P)_r$ and $(B)_r$ are the concentrations permitting study of the reverse reaction.

In a single reaction mixture, evolving naturally toward equilibrium, necessarily $(P)_f = (P)_r$ and $(B)_f = (B)_r$; applying detailed balance as before then yields $v_f/v_r' = v_r/v_r'$. That is, the two paths are equally favored in the two directions. However, if the kinetics are studied "irreversibly", first in one direction then in the other, by judiciously changing the conditions, this conclusion is not valid; the reaction might proceed preferentially by one path in one "irreversible" direction, and by the other in the reverse direction. This is true even although the local equilibrium flux interpretation has been admitted for the elementary rate constants.

G. Oscillating Reactions

A mechanistic network of first-order reactions may be described kinetically by a matrix equation analogous to the microscopic master equation, eq 76. As a consequence of detailed balance, it may be deduced²⁵ that the eigenvalues of the macroscopic transport matrix are all real-valued. Thus, there are no oscillatory components in the approach to equilibrium for such a system.²⁵

Other restrictions on this conclusion, besides that of first-order kinetics, are that the system is closed, homogeneous, and at constant temperature and constant volume. The conditions under which breakdown of one or more of these restrictions could lead to chemical oscillations has been the subject of considerable theoretical^{23,25} and experimental¹¹⁷ work. This subject is somewhat removed from the present one, and those interested may be referred elsewhere¹¹⁷ for an up-to-date review.

H. Relaxation Kinetics

The mathematical model used in section III is formally similar to that used in determining theoretical expressions for relaxation times in multistep kinetics studied by relaxation techniques. The transport matrix (eq 76) now defines the time evolution of chemical species, rather than of internal states of species, and the required relaxation times are the reciprocals of the eigenvalues. Since excellent coverage of this material is already available,¹²⁷ it will not be dealt with here. The closest analogy with the present work is probably with the $\text{Cl} + \text{H}_2 \rightleftharpoons \text{H} + \text{HCl}$ system, discussed above in section IV.D.

V. Summary

The conclusions expressed in section II of this review are purely empirical, in the sense that they are logical consequences of phenomenological equations found to offer an adequate account of the evolution of chemical systems to equilibrium. On the other hand, a major portion of the present work has been concerned with a theoretical justification of the chemical principle of detailed balance in cases where this is not a purely empirical result. As has been shown, the emergence of chemical kinetics, from the theoretical physics of nonequilibrium systems, is far from straightforward; in particular, two broad classes of theories of chemical kinetics have been considered, namely the local-equilibrium theory and the nonequilibrium eigenvalue approximation. These theories have been considered in very general, nonspecific terms, since the connection between detailed balance and microscopic reversibility is a very fundamental question, independent of the details of any particular version of either type of theory. For this reason this work is not, and is not intended to be, a review of modern analytical theories of chemical kinetics, all of which fall into one or other of the two classes discussed; to an even greater extent, the present work has ignored details of modern numerical theories, involving trajectory calculations, etc. Rather, an attempt has been made to trace the roots of detailed balance back to the time-reversal symmetry of the equation of motion in nonrelativistic quantum mechanics, by the most direct and general means possible. An attempt to display the logical form of the present work has been made in Figure 4.

VI. Appendix

A. Solution of Deterministic Multilevel Model

The derivation of the solution (eq 76) to the deterministic model (eq 76) will be outlined here. The first step is to transform the transport matrix K to a symmetric matrix S , for reasons which will become clear later; it is convenient to define a diagonal matrix X , such that $X_{ii} = x_i^*$, the equilibrium fractional

population of state i . Then, premultiplying both sides of eq 76 by $X^{-1/2}$ gives:

$$(d/dt)|w(t)\rangle = -X^{-1/2}KX^{1/2}X^{-1/2}|x(t)\rangle = -S|w(t)\rangle \quad (A1)$$

where $S = X^{-1/2}KX^{1/2}$ is related to K by a similarity transform, and $w_i = (x_i^*)^{-1/2}x_i$. The matrix S is symmetric, as a consequence of microscopic reversibility (eq 74), since:

$$\begin{aligned} S_{ij} &= \sum_{j=i}^n k_{ij}, \text{ and } -S_{ij}(i \neq j) = k_{ji}(x_j^*/x_i^*)^{1/2} \\ &= k_{ij}(k_{ij}/k_{ji})^{1/2} \\ &= k_{ij}(k_{ji}/k_{ij})^{1/2} \\ &= k_{ij}(x_i^*/x_j^*)^{1/2} = -S_{ji} \end{aligned} \quad (A2)$$

Then, the eigenvalues λ_r of S are real valued, and provided that these eigenvalues are nondegenerate, the corresponding eigenvectors $|\xi_r\rangle$ are orthogonal. Since S and K are related by a similarity transform, they have the eigenvalues λ_r in common, and the eigenvectors $|\phi_r\rangle$ of K , which are not in general orthogonal, are related to those of S by:

$$|\phi_r\rangle = X^{1/2}|\xi_r\rangle \quad (A3)$$

By suitable normalization, we may write:

$$\langle \xi_r | \xi_s \rangle = \delta_{rs} \quad (A4)$$

Since the $|\xi_r\rangle$ are a complete set, we can expand $|w(t)\rangle$ as a linear combination:

$$|w(t)\rangle = \sum_{r=1}^n c_r(t)|\xi_r\rangle \quad (A5)$$

where the coefficients c_r are to be determined as functions of the time t . This is best done by considering the time derivative of eq A5:

$$(d/dt)|w\rangle = \sum_{r=1}^n [(dc_r/dt)|\xi_r\rangle] \quad (A6)$$

Using eq A1, another expression may be obtained:

$$(d/dt)|w\rangle = -S|w\rangle = -S \sum_{r=1}^n c_r|\xi_r\rangle = -\sum_{r=1}^n (c_r\lambda_r|\xi_r\rangle) \quad (A7)$$

Combining eq A6 and eq A7 gives:

$$\sum_{r=1}^n [(dc_r/dt)|\xi_r\rangle] = -\sum_{r=1}^n [c_r\lambda_r|\xi_r\rangle] \quad (A8)$$

Premultiplying by $\langle \xi_r |$, and using the orthonormal relationship eq A4, gives:

$$dc_r/dt = -c_r\lambda_r, \text{ for } 1 \leq r \leq n \quad (A9)$$

whence

$$c_r(t) = c_r^0 \exp(-\lambda_r t) \quad (A10)$$

where c_r^0 is the ($t = 0$) value of $c_r(t)$. The n constants c_r^0 are defined by the initial conditions of the experiment, since from eq A5:

$$|w(0)\rangle = \sum_{r=1}^n c_r^0|\xi_r\rangle = \chi|C^0\rangle \quad (A11)$$

where χ is a modal matrix of S , such that the columns of χ are the column eigenvectors $|\xi_r\rangle$ of S . Substituting eq A10 into eq A5 now gives:

$$|w(t)\rangle = \sum_{r=1}^n [c_r^0|\xi_r\rangle \exp(-\lambda_r t)] \quad (A12)$$

By premultiplying by $X^{1/2}$, we may transform eq A12 to:

$$|x(t)\rangle = \sum_{r=1}^n [c_r^0|\phi_r\rangle \exp(-\lambda_r t)] \quad (A13)$$

Now, it is clear that for the special case $|x(t)\rangle = |x^*\rangle$ (the equilibrium composition):

$$(d/dt)|x^*\rangle = |0\rangle = -K|x^*\rangle \quad (A14)$$

so that $|x^*\rangle$ is an eigenvector of K with zero eigenvalue; for convenience, write $\lambda_1 = 0$, $|\phi_1\rangle = |x^*\rangle$. As a consequence, eq A13 may be written:

$$x_i(t) = x_i^* + \sum_{r=2}^n [c_r^0\phi_r(t) \exp(-\lambda_r t)], \quad 1 \leq i \leq n \quad (77)$$

B. Solution of Approximate Model of Widom^{82,83}

In this Appendix, the main assumptions of Widom's elucidation^{82,83} of the eigenvalue spectrum, the identification of chemical species, and detailed balance will be described in more detail than in the main text. The continuum analogue of eq 75 is:

$$\begin{aligned} dn(x,t)/dt &= \int_{-\infty}^{+\infty} w(y,x)n(y,t) dy \\ &\quad - \int_{-\infty}^{+\infty} \delta(y-x) \left[\int_{-\infty}^{+\infty} w(x,z) dz \right] n(y,t) dy \end{aligned} \quad (B1)$$

$n(x,t)$ is the fractional population in state x at time t ; the continuous index x is assumed to vary between $-\infty$ and $+\infty$, for later comparison with the quantum chemistry analogy. $w(x,y)dy$ is the probability per unit time that a molecule in state x will undergo a transition to a state in the range y to $y + dy$; thus $w(x,y)$ is the continuum analogy to k_{ij} in eq 75. The second term in eq B1 is written using the Dirac delta function $\delta(y-x)$, thus permitting retention of y as the chief integrating variable on the right-hand side.

Now, as in the discrete case (Appendix A), we transform eq B1 in such a way as to make the transition probabilities symmetrical with respect to an interchange of x and y :

$$\begin{aligned} w_s(x,y) &\equiv [f(x)/f(y)]^{1/2} w(x,y) \\ &= [f(y)/f(x)]^{1/2} w(y,x) \end{aligned} \quad (B2)$$

where $f(x)$ is the Boltzmann (equilibrium) value of $n(x,t)$, and the microscopic reversibility relation has been used. Now, by straightforward substitution, eq B1 becomes:

$$\begin{aligned} (d/dt)[n(x,t)/\sqrt{f(x)}] &= \int_{-\infty}^{+\infty} [w_s(y,x)n(y,t)/\sqrt{f(y)}] dy \\ &\quad - \int_{-\infty}^{+\infty} \delta(y-x) \left[\int_{-\infty}^{+\infty} w_s(x,z) \left\{ \frac{f(z)}{f(x)} \right\}^{1/2} dz \right] \frac{n(y,t)}{\sqrt{f(y)}} dy \\ &= - \int_{-\infty}^{+\infty} \kappa(y,x)[n(y,t)/\sqrt{f(y)}] dy \end{aligned} \quad (B3)$$

where the kernel $\kappa(y,x)$ is defined by:

$$\begin{aligned} -[\kappa(y,x)] &\equiv w_s(y,x) - \delta(y-x) \\ &\quad \times \left[\int_{-\infty}^{+\infty} w_s(x,z) \left\{ \frac{f(z)}{f(x)} \right\}^{1/2} dz \right] \end{aligned} \quad (B4)$$

where the negative sign has been included to ensure positive eigenvalues as in Appendix A. Clearly, $\kappa(y,x) = \kappa(x,y)$; this is the analogue of the result that the matrix S of Appendix A is symmetric, and follows directly from microscopic reversibility. Then, the eigenvalue equation for $\kappa(y,x)$

$$\begin{aligned} \lambda_r \psi_r(x) + \int_{-\infty}^{+\infty} \kappa(y,x)\psi_r(y) dy &= \int_{-\infty}^{+\infty} \left\{ \delta(y-x) \right. \\ &\quad \times \left. \int_{-\infty}^{+\infty} w_s(x,z) \left\{ \frac{f(z)}{f(x)} \right\}^{1/2} dz - w_s(y,x) \right\} \psi_r(y) dy \end{aligned} \quad (B5)$$

must have real eigenvalues λ_r and orthogonal eigenfunctions ψ_r .

Equation B5 may be reduced to a simpler form as follows

(considering only the second term at present):

$$\begin{aligned} & \int_{-\infty}^{+\infty} \delta(y-x) \left\{ \psi_r(y) \left[\int_{-\infty}^{+\infty} (x,z) [\tilde{f}(z)/\tilde{f}(x)]^{1/2} dz \right] \right\} dy \\ &= \psi_r(x) \int_{-\infty}^{+\infty} \{ w_s(x,z) [\tilde{f}(z)/\tilde{f}(x)]^{1/2} \} dz \\ &= \psi_r(x) \int_{-\infty}^{+\infty} \{ w_s(x,y) [\tilde{f}(y)/\tilde{f}(x)]^{1/2} \} dy \quad (\text{B6}) \end{aligned}$$

where the second line follows from the first since the Dirac delta function is such that $\int_{-\infty}^{+\infty} g(x)\delta(x-a)dx = g(a)$, and the third line follows since z is just a dummy variable which labels the states in the same fashion as x or y . Then, substitution of eq B6 into eq B5, using the microscopic reversibility relation $w_s(y,x) = w_s(x,y)$, gives as the eigenvalue equation for the symmetrized kernel:

$$\lambda_r \psi_r(x) = \int_{-\infty}^{+\infty} w_s(y,x) \{ [\tilde{f}(y)/\tilde{f}(x)]^{1/2} \psi_r(x) - \psi_r(y) \} dy \quad (\text{B7})$$

Equation B7 is crucial in Widom's treatment;^{82,83} before further reducing this equation, we note that the kinetic analysis now proceeds by direct analogy with the discrete case outlined in Appendix A. Thus, $[n(x,t)/\sqrt{\tilde{f}(x)}]$ is expanded as a linear combination of the orthogonal basis set of eigenfunctions $\psi_r(x)$ (it is clear from inspection of eq B7 that $\psi_1(x) \equiv \sqrt{\tilde{f}(x)}$ is an eigenfunction with eigenvalue $\lambda_1 = 0$). Then, ordering the eigenvalues so that $0 = \lambda_1 < \lambda_2 < \lambda_3 < \dots$, the solution to eq B1 may be written as:

$$n(x,t) = \tilde{f}(x) + \sum_{r>1} [c_r \sqrt{\tilde{f}(x)} \psi_r(x) \exp(-\lambda_r t)] \quad (\text{B8})$$

where, as before, the constants c_r depend upon the initial conditions $n(x,0)$. Equation B8 is the continuum analogue of eq 77 for the discrete case; again, this is the point at which chemical classifications must be imposed upon what is thus far a purely physical solution. Thus, it is assumed that it is possible to assign the states to chemical species, e.g.,

$$n_A(t) \equiv \int_A n(x,t) dx, \text{ etc.} \quad (\text{B9})$$

It is, of course, the purpose of the present approach^{82,83} to attempt to clarify the implications of such chemical classifications. It is clear, however, that the previous analysis of the discrete model applies to the present continuum case, with obvious replacements of summations by integrations. In particular, the same impasse is reached with regard to detailed balance in the closed-loop scheme eq 91, in terms of the eigenvalue approximation; moreover, there is still no justification for assuming conditions on the eigenvalues like eq 87 and eq 95. To do this, it is necessary to return to the eigenvalue equation, eq B7; following Widom,^{82,83} an approximate, but physically realistic, form of this equation is derived.

First, define $F(y) \equiv \{ [\tilde{f}(y)/\tilde{f}(x)]^{1/2} \psi_r(x) - \psi_r(y) \}$ (see eq B7), and expand $F(y)$ as a Taylor series about $y = x$, thus: $F(y) = \sum_{m=0}^{\infty} [(1/m!) F^{(m)}(x) (y-x)^m]$ (m integral), where $F^{(m)}(x)$ is the m th derivative of $F(y)$, evaluated at $y = x$. Then we have:

$$\begin{aligned} F(y) = 0 + & \{ [\sqrt{\tilde{f}(x)'} / \sqrt{\tilde{f}(x)}] \psi_r(x) - \psi_r'(x) \} (y-x) \\ & + \frac{1}{2} \{ [\sqrt{\tilde{f}(x)''} / \sqrt{\tilde{f}(x)}] \psi_r(x) - \psi_r''(x) \} (y-x)^2 \\ & + \dots \quad (\text{B10}) \end{aligned}$$

$F(y)$ is the multiplier of $w_s(y,x)$ in the integrand of eq B7, and primes here denote differentiation with respect to x ; by substituting eq B10 into eq B7, and noting that M_m , the m th moment of $w_s(y,x)$, is given by:

$$M_m \equiv \int_{-\infty}^{+\infty} [w_s(y,x) (y-x)^m] dy$$

the eigenvalue equation for $\kappa(y,x)$ becomes:

$$\begin{aligned} M_1 \{ & [\sqrt{\tilde{f}(x)'} / \sqrt{\tilde{f}(x)}]^{1/2} \psi_r(x) - \psi_r'(x) \} \\ & + \frac{1}{2} M_2 \{ [\sqrt{\tilde{f}(x)''} / \sqrt{\tilde{f}(x)}]^{1/2} \psi_r(x) - \psi_r''(x) \} + \dots \\ & = \lambda_r \psi_r(x) \quad (\text{B11}) \end{aligned}$$

The first approximation is now to assume that the third and higher moments may be ignored; this clearly implies that the $w_s(x,y)$ values be significant only for $y \approx x$. As emphasized in the main text, this in turn requires that the index x (or y) be a smoothly varying function of the internal energy of the reactant molecule, in order that the approximation be physically realistic.

As a second approximation, it is assumed that the first moment M_1 is much smaller than M_2 . If $w_s(x,y)$ were symmetric, in the sense that $w_s(x, x+\delta x) = w_s(x, x-\delta x)$, the first moment M_1 would be zero. Obviously this is unlikely ever to be true, but it is possible to suggest that, under the same condition that the higher moments may be ignored (see above), M_1 should be very small. To see the extent to which this claim may be justified, consider the ratio:

$$\begin{aligned} \frac{w_s(x, x+\delta x)}{w_s(x, x-\delta x)} & \equiv \left[\frac{\tilde{f}(x)/\tilde{f}(x+\delta x)}{\tilde{f}(x)/\tilde{f}(x-\delta x)} \right]^{1/2} \\ & \times \left[\frac{w(x, x+\delta x)}{w(x, x-\delta x)} \right] \approx \left[\frac{e^{+\Delta\epsilon/kT}}{e^{-\Delta\epsilon/kT}} \right]^{1/2} [e^{-\Delta\epsilon/kT}] = 1.0 \end{aligned}$$

where $\Delta\epsilon$ is the internal energy difference associated with *both* $\pm\delta x$ (δx and $\Delta\epsilon$ small); we have ignored differences in statistical weights for the Boltzmann ratios, and also differences in preexponential factors for the transition probabilities. It is also assumed that the deexcitation process $x \rightarrow x - \delta x$ proceeds without activation energy.

Thus, under a single physical assumption, it is at least reasonable to approximate eq B11 by including only the term in M_2 :

$$\begin{aligned} (-\frac{1}{2} M_2) \psi_r''(x) + & \{ \frac{1}{2} M_2 [\sqrt{\tilde{f}(x)''} / \sqrt{\tilde{f}(x)}] \} \psi_r(x) \\ & = \lambda_r \psi_r(x) \quad (\text{B12}) \end{aligned}$$

Equation B12 bears a striking formal resemblance to a Schrodinger equation;^{82,83} if the state index x is reinterpreted as a position coordinate, and the following formal analogies are made:

$$M_2 \equiv (\hbar^2/\mu); \quad \frac{1}{2} M_2 [\sqrt{\tilde{f}(x)''} / \sqrt{\tilde{f}(x)}] \equiv V(x) \quad (\text{B13})$$

then eq B12 corresponds to the Schrodinger equation for motion of a particle of mass μ in a one-dimensional potential $V(x)$, with energy eigenvalue λ_r and wave function $\psi_r(x)$. Clearly, $\lambda_1 = 0$, $\psi_1(x) = \sqrt{\tilde{f}(x)}$ is a solution, and we already know that $\lambda_1 = 0$ is the smallest eigenvalue; i.e., $\psi_1(x)$ is the ground state wave function. Having reached this analogy, it is now necessary to investigate the form of the potential $V(x)$; while M_2 is indeed a function of x , it is clear that the functional form of $V(x)$ will be dominated by that of $[\sqrt{\tilde{f}(x)''} / \sqrt{\tilde{f}(x)}]$. The general form of this function is shown graphically as Figure 2 in the main text. The "dissociation limits" arise basically because the continuous index of states x was chosen to run between $-\infty$ and $+\infty$. The somewhat indefinite zero for x lies somewhere near the energy maximum in Figure 1, at the chemical A-B boundary.

The "potential" $V(x)$ is now considered to be written as follows:

$$V(x) = V_A(x) + V_B(x) + V_{AB}(x) \quad (\text{B14})$$

where it is assumed that both $V_A(x)$ and $V_B(x)$ go to infinity at $x = 0$; $V_{AB}(x)$ is the perturbation interaction between the two wells corresponding to A and B. This picture is ideally suited to a discussion in terms of the "resonance" phenomenon.¹¹⁸

First, it is possible to account for the nature of the eigenvalue spectrum, described by eq 87. This is easiest to see if the "resonance" is "exact", i.e., if the wells corresponding to A and B are identical; then for the unperturbed system (i.e., $V_{AB}(x)$ set

to zero in eq B14), the ground state would correspond to two degenerate energy levels, one belonging to each well. When the perturbation V_{AB} is "switched in", thus permitting interaction between the two wells, these two degenerate levels split, by an amount controlled by the magnitude of V_{AB} relative to the depths of the V_A and V_B wells. If the barrier separating the two wells is high (in terms of the fictional potential $V(x)$ of Figure 2, *not* directly in terms of the *real* potential $U(\theta)$ of Figure 1), this splitting will be small, relative to the gap between the unperturbed eigenvalues; that is to say, the eigenvalue spectrum is like that required by eq 87. The fact that there are *two* small, almost degenerate eigenvalues corresponds to the fact that there are *two* wells, i.e., two chemical species, A and B.

The ground-state eigenfunction $\psi_1(x) = \sqrt{f(x)}$ has appreciable values in both wells, since at equilibrium there are significant quantities of both A and B (i.e., reaction is reversible, in the colloquial sense); in order to deduce the chemical principle of detailed balance, a particular orthogonality property of the eigenfunctions is required.⁸³

Following Bartis and Widom,⁸³ the ground-state wave function $\psi_1(x)$ is written thus:

$$\psi_1(x) = \sqrt{f(x)} = \theta_A(x) + \theta_B(x) \quad (\text{B15})$$

where θ_A is equal to ψ_1 over that range of x defined as corresponding to species A, and is zero elsewhere; θ_B is similarly defined. Then, in order that θ_A and θ_B be continuous, well-behaved functions, the arbitrary boundary drawn between A and B must fall in that range of x where $\sqrt{f(x)}$ is zero, or almost zero. That is to say, this boundary *must* be chosen, in accord with chemical intuition, near the maximum of the *real* potential energy diagram, Figure 1.

We now use θ_A and θ_B as a linearly independent basis set; their linear independence follows from their definition. The vector space spanned by the θ 's is clearly of dimension equal to the number of chemical species involved in the reaction (two in the present case). Thus, we choose to expand the two eigenfunctions corresponding to the two smallest eigenvalues (i.e., the almost degenerate eigenvalues) in terms of the basis set θ_A and θ_B :

$$\psi_r(x) = \gamma_{A,r}\theta_A + \gamma_{B,r}\theta_B \quad (\text{B16})$$

where, for $r = 1$, $\gamma_{A,r} = 1 = \gamma_{B,r}$ (eq B15).

For convenience,⁸³ define quantities $\alpha_{A,r}$ by:

$$\begin{aligned} \alpha_{A,1} &\equiv \int_A [\psi_1(x)]^2 dx = \int_A \theta_A^2 dx = \int_{-\infty}^{+\infty} \theta_A^2 dx \\ \alpha_{A,2} &= C_2^0 \int_A [\psi_1(x)\psi_2(x)] dx = C_2^0 \\ &\times \int_A [\theta_A(x)\gamma_{A,2}\theta_A(x)] dx = C_2^0\gamma_{A,2} \int_{-\infty}^{+\infty} \theta_A^2 dx \quad (\text{B17}) \end{aligned}$$

so that eq B16 becomes:

$$\psi_r(x) = (\alpha_{A,r}/C_r^0\alpha_{A,1})\theta_A(x) + (\alpha_{B,r}/C_r^0\alpha_{B,1})\theta_B(x)$$

Now, the eigenfunctions $\psi_r(x)$ are orthogonal and may be assumed normalized without loss of generality. In terms of the quantum-mechanical analogy to eq B12, this orthogonality arises because the Hamiltonian is hermitian; in terms of the true interpretation of eq B12, this corresponds to the fact that the kernel $\kappa(x,y)$ is symmetric, which in turn is a direct consequence of microscopic reversibility. Thus:

$$\begin{aligned} \int_{-\infty}^{+\infty} \psi_r\psi_s dx &= \int_A \psi_r\psi_s dx + \int_B \psi_r\psi_s dx \\ &= \int_A \left(\frac{\alpha_{A,r}\alpha_{A,s}}{C_r^0C_s^0\alpha_{A,1}^2} \right) \theta_A^2 dx \\ &\quad + \int_B \left(\frac{\alpha_{B,r}\alpha_{B,s}}{C_r^0C_s^0\alpha_{B,1}^2} \right) \theta_B^2 dx \quad (\text{B18}) \end{aligned}$$

i.e.,

$$\left[\frac{\alpha_{A,r}^2 + \alpha_{B,r}^2}{\alpha_{A,1}} \right] (C_r^0)^2 \delta_{rs} = \left(\frac{\alpha_{A,r}\alpha_{A,s}}{\alpha_{A,1}} \right) + \left(\frac{\alpha_{B,r}\alpha_{B,s}}{\alpha_{B,1}} \right)$$

Equation B18 is the crucial orthogonality relation of Bartis and Widom.⁸³ Note that it is an approximate result only, in that it arises from the same approximate treatment which explains the qualitative features of the eigenvalue spectrum, and that it depends on microscopic reversibility plus chemical intuition, i.e., external to, but consistent with, the purely physical description of the system.

The above derivation applies directly only to a two-species case (A and B). Extension to three or more species is possible but involves⁸³ multidimensional Schrodinger equations analogous to eq B12; i.e., it is necessary to use more than one index to label the states. However, the same conclusions apply; because the number of wells in resonance, in the quantum-mechanical analogy, is equal to the number of chemical species in the kinetic problem, this is also the number of nearly degenerate eigenvalues equal to or near zero. Orthogonality relations like eq B18 may be similarly derived:

$$\sum_x (\alpha_{x,r}\alpha_{x,s}/\alpha_{x,1}) = \delta_{r,s} [(C_r^0)^2/\alpha_{x,1}] \sum_x (\alpha_{x,r}^2) \quad (\text{B19})$$

where \sum_x denotes summation over all the chemical species, which in turn are defined as regions lying between points where $\sqrt{f} \approx 0$.

If now there are m chemical species, after the short transient time $(\lambda_m - \lambda_{m+1})^{-1}$, the solution to eq B3 is readily shown to be:

$$n_A(t) = \int_A m(x,t) dx = \sum_{r=1}^m \alpha_{A,r} \exp(-\lambda_r t) \quad (\text{B20})$$

where the initial conditions are now contained in the $\alpha_{A,r}$ (eq B17), and similarly for $n_B(t)$, etc. Comparison with the relevant phenomenological rate equations, as in eq 96 in the main text, yields the following expression for the rate constants (after simplification using the orthogonality relation eq B19):

$$k_{AB}^\lambda = (K_{AB})^{1/2} \sum_{r=2}^m [\lambda_r g_{A,r} g_{B,r}], \text{ etc.} \quad (\text{B21})$$

where

$$g_{A,r} = (\alpha_{A,r}/\sqrt{\alpha_{A,1}}) / \left\{ \sum_x [\alpha_{x,r}/\sqrt{\alpha_{x,1}}]^2 \right\}^{1/2} \quad (\text{B22})$$

where the C_r^0 in $\alpha_{A,r}$ and $\alpha_{x,r}$ cancel. The rate constants defined by eq B21 are thus independent of time and of the initial conditions, and also obey detailed balance.

Finally, the orthogonality relation eq B19 will be transformed into the terminology appropriate to the discrete model discussed in the text. This involves a reinterpretation of the $\alpha_{x,r}$ quantities. Clearly:

$$\begin{aligned} \alpha_{A,1} &= \int_A [\psi_1(x)]^2 dx = \int_A [\sqrt{f(x)}]^2 dx \equiv \sum_A f_i = a^* \\ \alpha_{A,r} &= C_r^0 \int_A \psi_1\psi_r dx \\ &= C_r^0 \int_A \sqrt{f(x)}\psi_r(x) dx \equiv C_r^0 \sum_{i=1}^{l-1} (x_i^*)^{1/2} \xi_r(i) \quad (\text{B23}) \end{aligned}$$

i.e.

$$\begin{aligned} \alpha_{A,r} &\equiv C_r^0 \sum_{i=1}^{l-1} \phi_r(i) = C_r^0 u_r \\ \alpha_{B,r} &= C_r^0 v_r, \text{ etc.} \quad (\text{B24}) \end{aligned}$$

where the notation used in eq B24 corresponds to that used in Appendix A and in eq 96 of the main text. Then, for the three

species case, for example, the orthogonality relation eq B19 becomes:

$$(u_r u_s / a^*) + (v_r v_s / b^*) + (z_r z_s / c^*) = 0, r \neq s \quad (99)$$

Note that for $r = 1$ or $s = 1$, the above relationship holds *exactly*, without the need for the above justification devised by Bartis and Widom,⁸³ since in such a case the relation becomes (for $s = 1$):

$$u_r + v_r + z_r = 0 = \sum_{i=1}^n \phi_r(i), r \neq 1$$

which is guaranteed by mass conservation in any case.^{69,70} In the case of just two species, therefore, the orthogonality relation eq B19 is exact and does *not* represent a new result, unobtainable from purely macroscopic considerations. Thus, in the two-species case, microscopic reversibility (via eq B19) is not necessary to justify detailed balance, thus confirming the conclusions of section II.B.

One point which was not properly discussed above concerns the dependence of the second moment M_2 upon the state label x (see paragraph following eq B12). In order for eq B12 to be useful, it is necessary that this dependence of M_2 upon x be extremely weak, relative to that of the remaining factor on the left side of eq B12; thus, the formal analogies of eq B13 assume M_2 to be effectively constant. Recently, an attempt has been made¹²⁸ to investigate the physical significance of these and other mathematical approximations in the model of Widom.^{82,83} While this attempt has not proved to be completely satisfactory,¹²⁸ it has succeeded in demonstrating that the mathematical model is at least physically reasonable. Moreover, the same model^{82,83} without further embellishment was shown¹²⁸ to account for a "linear mixture formula" applicable to a simple isomerization reaction occurring in mixtures dilute in reactant, but containing more than one heat-bath molecule; in particular, the effective constancy of M_2 played a crucial role in this regard. The main experimental evidence for the validity of a "linear mixture formula" as a rate law, under *nonequilibrium* conditions, involves dissociation-recombination reactions of diatomic molecules; unfortunately, the simple theory does not apply directly to such cases, and further approximations were necessary¹²⁸ in order to extend the theoretical conclusions to cover the cases of experimental interest. Nonetheless, it is remarkable that Widom's model^{82,83} can illuminate simultaneously so many aspects of nonequilibrium kinetics.

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