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THE RELATIONSHIP BETWEEN FORWARD AND REVERSE REACTION RATES UNDER NON-EQUILIBRIUM CONDITIONS

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ABSTRACT

It is shown that for a given elementary reaction and under non-equilibrium conditions, the ratio of the rate constant of the forward reaction to the rate constant for the reverse reaction is equal to the equilibrium constant, provided (a) both forward and reverse reaction take place under the same experimental conditions, and (b) products and reactants establish independent equilibrium distributions of states to the transition complex of the reaction. The proof applies even if the activity coefficients of reactants, products, and activated complexes are different from their equilibrium values and if the rate limiting step is different from that when the reaction is at equilibrium. One consequence of this proof is that vaporization and condensation coefficients must be equal for any specified non-equilibrium conditions.
I. INTRODUCTION

Our attention was attracted to the problem of establishing the quantitative relationship between vaporization coefficients and condensation coefficients for non-equilibrium and thermodynamically non-ideal systems when, in the course of adapting a model for vaporization kinetics (2)(3) to an analysis of the kinetics of decomposition reactions, two of us derived an expression for the effect of a porous layer on the decomposition rate. (4) The expression depends on the condensation coefficient $a_c$ -- that is, on the fraction of those molecules striking a surface that traverse any barrier to the condensation process.

The condensation coefficient is difficult to measure directly, although the vaporization coefficient $a_v$ -- that is, the ratio of the measured vapor flux from a surface to the maximum possible flux calculated from the Hertz-Knudsen-Langmuir equation--can readily be obtained from experimental measurements of rates of vaporization in vacuum.(2)(3)

By the principle of microscopic reversibility, the condensation coefficient must be equal to the vaporization coefficient at equilibrium. But because the principle of microscopic reversibility cannot be assumed for non-equilibrium conditions, Paule and Margrave (5) have warned against assuming the equality $a_v = a_c$ in those effusion studies in which the pressure is reduced below the equilibrium value. Ackermann, Thorn and Winslow (6) have noted that "although the vaporization coefficient must equal the condensation coefficient if the gas and the condensed phase are at equilibrium, nothing requires that they be equal if the gaseous and condensed phases are at different temperatures." They developed a model which yields a temperature-independent vaporization...
coefficient but a temperature-dependent condensation coefficient.

Our intuitive judgment, despite these assessments, was that under fixed experimental conditions the vaporization and condensation coefficients must be equal, so that, in the case of the porous desorption barrier, the experimentally determined vaporization coefficient could be substituted for the condensation coefficient under the same experimental conditions. To test this judgment, we determined to examine the general question of when the rate constant of a forward reaction and the rate constant for the reverse reaction can be quantitatively related through the Gibbs free energy of the overall reaction.

By definition $\alpha_v = J_v / J_e$ and $\alpha_c = J_c / J_s$ where $J_v$ is the flux per unit time per unit area of molecules of the condensed phase that successfully traverse any barrier to vaporization and leave the surface, $J_c$ is the flux of vapor molecules that successfully traverse any barrier to condensation, $J_s$ is the total flux of vapor that strikes the surface when the pressure has some arbitrary value $P$, and $J_e$ is the total flux of molecules that strike the surface if it is exposed to vapor at its equilibrium pressure $P_e$. From the kinetic theory of gases the flux $J_s$ for any gas pressure $P$ can be calculated to be

$$J_s = \frac{P}{(2\pi MR_T)^{1/2}}$$  \hspace{1cm} (1)

where $M$ is the molecular weight of the vapor molecule, $R$ is the gas constant and $T$ is the absolute temperature. Equation (1) yields $J_e$ when the pressure is the equilibrium pressure $P_e$. 
Using standard formulations of reaction kinetics (7), it can be shown that for \( \alpha_v \) to be equal to \( \alpha_c \) requires (2)

\[
\frac{\kappa_v \nu_v \exp (-\Delta G_v^*/RT)}{\kappa_c \nu_c \exp (-\Delta G_c^*/RT)} = \exp (-\Delta G_v^0/RT)
\]

where \( \kappa_v, \nu_v \) and \( \Delta G_v^* \) are the transmission coefficient, the frequency factor and the free energy of activation for the vaporization process, \( \kappa_c, \nu_c \) and \( \Delta G_c^* \) the corresponding quantities for the condensation process, and \( \Delta G_v^0 \) the standard free energy of vaporization. The formulation of the rate equations used here corresponds to the thermodynamic form given by Johnston (7). In more general terms, Eq. (2) may be written

\[
\frac{k_f}{k_r} = K_{eq} = \exp (-\Delta G_n^0/RT)
\]

where \( k_f \) and \( k_r \) are the rate constants for the forward and reverse reactions for which \( K_{eq} \) is the equilibrium constant and \( \Delta G_n^0 \) the standard free energy change in the forward direction. If Eq. (2) can be proved for non-equilibrium conditions, then the equality \( \alpha_c = \alpha_v \) is proved for non-equilibrium conditions.

The principle of microscopic reversibility (8) requires the equalities expressed by Eq. (3) at equilibrium, and experimental verification of the relationship to within reasonable error limits has been obtained for particular reactions far from equilibrium (9). But theoretical proofs of the relation apparently have been given only for cases
in which the activity coefficients of all reactants, products, and possible catalysts remain identical to their values at equilibrium (10)(11)(12).

The most general proof is probably that of Rice (10), who established Eq. (3) for steady state non-equilibrium conditions. Rice's proof assumes that the reaction environment is held essentially constant, that is, unchanged between equilibrium and the non-equilibrium conditions of the proof, and the rate constants for forward and reverse reactions are independent of concentrations of reactants and products over the experimental range that he and others (11)(12) considered by means of his general analysis.

Rice's proof justifies use of Eq. (3), for example, for the analysis of low pressure gas-phase reactions, but does not prove the equation when the barrier to reaction may be different from the barrier under equilibrium conditions. Surface morphology, and therefore the concentration of active surface sites, is known sometimes to change markedly when a crystal undergoes free vaporization from the morphology developed in the presence of the saturated vapor. Consequently, it is clearly possible for a different reaction step to be rate limiting under free vaporization conditions from that which limits the reaction rate as an equilibrium vapor concentration is approached. Similar possibilities exist in solution reactions for which the reactant and/or product concentrations are high. Furthermore, in solutions when concentrations of reactants or products are high and far from equilibrium, their presence may influence the dielectric strength enough to change the height of the barrier to reactions from the height that would be found under equilibrium conditions.
We wish, therefore, to derive the relationship between the forward and reverse reaction rates and the free energy difference between products and reactants without restriction on the concentrations of either products or reactants, although the concentration of activated complexes can be assumed to be low—the usual situation in reaction kinetics. The demonstration should be applicable whether the rate-limiting step under non-equilibrium conditions is the same or different from that under equilibrium conditions. We proceed by adopting transition state theory—in particular the assumption that the concentration of an activated complex in a given reaction direction is maintained at equilibrium with the reactants for that direction. It will be argued in the discussion section that for vaporization and condensation reactions the equilibrium assumption of transition state theory is an excellent approximation.

II. THEORETICAL DEVELOPMENT

The activated complex for the forward reaction by a particular reaction path is here defined as an aggregate of particles supplied by equilibration among the reactants and any possible catalysts to reaction such that the activated complex has (1) a thermal free energy (defined below) equal to or greater than the saddle point thermal free energy barrier to reaction and (2) a trajectory directed past the saddle point thermal free energy barrier in the direction of the reaction products. An activated complex for the reverse reaction over the same saddle point barrier is an aggregate of particles of the same composition and thermal free energy content as found in the activated complex for the forward reaction, but is produced by equilibration of products and possible
catalysts and has an opposite trajectory from the complex produced from reactants. The term "thermal free energy" as used here refers to the total free energy plus the product of the temperature and the configurational entropy (13). Thermal free energy changes are measures of the changes in average internal free energy content per particle. Under conditions of thermodynamic equilibrium, the relative concentrations, or pressures, of the various species are given by their differences in thermal free energies. For the case of the vaporization of a pure substance in the perfect gas range, for example, the thermal free energy change is just \(-RT \ln p = \Delta H^O_v - T\Delta S^O_v\).

It is assumed that both reactants and products of an elementary step are capable of establishing independently an equilibrium distribution of states up to and including any state that can undergo decomposition that would be irreversible, or partly so, in the absence of an equal or greater opposite flux from a second source. This equilibrium has to be clearly distinguished from complete thermodynamic equilibrium. In our nomenclature, activated complex implies a direction, transition state does not. The limited equilibrium assumption described at the beginning of this paragraph is customarily made in transition state theory for the forward reaction studied far from equilibrium (14)(15).

Suppose the net reaction to be considered is

\[
A + B = AB
\]  

(4)

where A and B are reactants, and AB is the reaction product. Suppose that one path for the reaction, not necessarily the principal path at
equilibrium, is

\[ A + B + C \xrightarrow{\text{**}} \text{ABC}^* \rightarrow AB + C \]  

(5)

where ABC* is the activated complex for this reaction path. Any reaction product in the system will establish an equilibrium distribution of accessible excited states and of products of reaction with matter in the system environment, and some activated complexes will be formed from the reaction product with trajectories which will carry these complexes back across the saddle point thermal free energy barrier.

The net rates of the forward and reverse reaction, \( J_f \) and \( J_r \), can be written

\[ J_f = \frac{d[X_{AB}]}{dt} = g_f [X_{\text{ABC}}]_{\text{th},f} \]  

(6)

\[ J_r = -\frac{d[X_{AB}]}{dt} = g_r [X_{\text{ABC}}]_{\text{th},r} \]  

(7)

where \([X_{\text{ABC}}]_{\text{th},f}\) and \([X_{\text{ABC}}]_{\text{th},r}\) are the concentrations of transition state species in thermodynamic equilibrium with reactants and products, \( g_f \) and \( g_r \) are proportionality constants to be evaluated later.

We can define a standard free energy \( \Delta G_f^0 \) for formation of the transition state from the reactants in their standard states and can define \( \gamma_r \) as the activity coefficient for the activated complex of the forward reaction. Then for equilibrium between the reactants and their transition state
\[ \Delta G_f^0 = -RT \ln \frac{\gamma_f [X_{ABC}]_{th,f}}{a_A^f a_B^f a_C^f} \]  

(8)

where the script \( a \)'s are activities relative to the same standard states for which the overall reaction (Eq. (4)) would have the standard free energy \( \Delta G_n^0 \). Similarly, for the reverse reaction

\[ \Delta G_r^0 = -RT \ln \frac{\gamma_r [X_{ABC}]_{th,r}}{a_A^r a_B^r a_C^r} \]  

(9)

Equations (8) and (9) can be used to eliminate the unknown composition of activated complex from Eqs. (6) and (7), yielding

\[ J_f = \epsilon_f a_B^f a_C^f \frac{a_A^f}{\gamma_f} \exp \left( -\Delta G_f^0/RT \right) \]  

(10)

and

\[ J_r = \frac{\epsilon_r a_B^r a_C^r}{\gamma_r} \exp \left( -\Delta G_r^0/RT \right) \]  

(11)

The terms other than the activities in these two equations constitute \( k_f \) and \( k_r \), the rate constants for the forward and reverse reactions. Dividing \( k_f \) by \( k_r \) gives

\[ \frac{k_f}{k_r} = \frac{\exp(-\Delta G_f^0/RT) \epsilon_f \gamma_r}{\exp(-\Delta G_r^0/RT) \epsilon_r \gamma_f} \]  

(12)
But the activated complexes for forward and reverse reactions have identical standard free energy contents, so $\Delta G_f^0 - \Delta G_r^0 = \Delta G_n^0$. And in any specified solution $\gamma_r = \gamma_f$, therefore

$$\frac{k_f}{k_r} = \exp \left( \frac{-\Delta G_n^0}{RT} \right) \frac{g_f}{g_r} \quad (13)$$

If the proportionality constants of Eqs. (6) and (7), $g_f$ and $g_r$, are equal to each other, Eq. (13) is identical to Eq. (3), the relationship between rates of forward and reverse reaction that we wish to prove.

Rice's "law of independence or non-interaction" (10) when applied to Eq. (13) leads to the conclusion that $g_f$ must equal $g_r$ in the solutions of fixed activity coefficients which he considered. But since we wish to examine the relationship between $g_f$ and $g_r$ under a wider range of conditions, we will undertake a more detailed examination than his of the implications of the principle of microscopic reversibility to non-equilibrium reaction conditions.

At equilibrium, the total forward flux $J_{ft}$ which crosses a saddle point thermal free energy barrier at any point, must exactly equal the total reverse flux $J_{rt}$ at the same point. The total forward flux will be the sum of several components, $j_f$, $j_r'$, and $\Sigma j_{fr}$, and the reverse flux will be the sum of several components $j_r$, $j_f'$ and $\Sigma j_{rf}$, where $j_f$ is the total flux of the specified activated complexes which are produced by equilibration among the reactants, $j_r$ is the corresponding total flux produced by equilibration among products, $j_f'$ is the flux of the activated complexes from the forward reaction that after crossing the barrier are
returned across the same barrier before having lost their activation energy by equilibration with the reaction products and $\Sigma j_{ri}^{O}$ is the flux of reactants that having crossed the thermal free energy barrier from reactants to products at other points are returning across the barrier at the point of interest without having lost a substantial part of their activation energy by equilibration with products. The terms $j_r$, $j'_r$, and $\Sigma j_{ri}^{O}$ have similar meaning for the products. If $X_f^*$ and $X_r^*$ are used to symbolize the concentration of activated complexes in the forward and reverse directions and $f$, $f'$, $\Sigma r_{ri}^{O}$, $r$, $r'$, and $\Sigma r_{ri}^{O}$ are proportionality constants between the concentrations and the fluxes which are identified with the same symbols, by the principle of microscopic reversibility the condition at equilibrium is

$$J_f = f X_f^* + r' X_r^* + \Sigma r_{ri}^{O} X_{ri}^* = r X_r^* + f' X_f^* + \Sigma r_{ri}^{O} X_{fi}^* = J_r \tag{14}$$

where $X_{fi}^*$ is the concentration of the $i$'th kind of activated complex for the forward reaction and $X_{ri}^*$ is the concentration of the same complex in the reverse reaction. But, for example,

$$r_{ri}^{O} X_{ri}^* = r_{ri} X_r^* \tag{15}$$

at equilibrium by the principle of microscopic reversibility, where $r_{ri}^{"}$ is the proportionality constant relating the flux of reactants crossing the thermal free energy barrier at the point of interest and subsequently returning across the different free energy barrier at the point characterized by the complexes of equilibrium concentration $X_{ri}^*$. 
Substituting equations of the form of (15) into (14) and rearranging yields

\[(f-f' - \sum_{i}^{\nu} f_i^\nu)X_f^* = (r-r' - \sum_{i}^{\nu} r_i^\nu)X_r^*\]  \hspace{1cm} (16)

At equilibrium \(X_f^* = X_r^*\), and therefore the principle of microscopic reversibility requires also at equilibrium that

\[f-f' - \sum_{i}^{\nu} f_i^\nu = r-r' - \sum_{i}^{\nu} r_i^\nu\]  \hspace{1cm} (17)

In a range of compositions in which activated complexes obey Henry's law, the complexes have negligible thermodynamic influence on each other. It is therefore to be expected that in the Henry's law range variations in the concentrations of the complexes will also have negligible influence on the constants of Eq. (17) which reflect the probabilities that individual complexes will undergo various possible transitions. The left hand side of Eq. (17) can be identified as \(g_f\), and the right hand side as \(g_r\), the constants in Eq. (13). It is proved, therefore, subject to the assumption next discussed, that Eq. (3) relates the rate constants for a forward and reverse reaction by any particular path to the standard free energy of reaction so long as the activated complexes by the various reaction paths are in the Henry's law concentration range.

A tacit assumption of the arguments so far presented is that the kinetic factors \(g_f\) and \(g_r\) of the rate expression are the same function of the activity coefficient, \(\gamma_f = \gamma_r\), of the activated complex. A
justification should be presented for the assumption.

The proof that has been given above demonstrates that for any one of the reaction paths that can be followed at equilibrium, and under Henry's law conditions for the activated complexes, \( g_f \) must equal \( g_r \) for that path independent of the concentration of the activated complexes for that and other paths. But the equality \( g_f = g_r \) must then be an attribute of any reaction path since there is no reason to expect that transition probabilities between states involved in a reaction path that happens not to be accessible under equilibrium conditions will be unequal when the transition probabilities are equal for all possible paths that happen to be accessible under equilibrium conditions. This conclusion is consistent with expectations from the law of dynamic reversibility, which has been proved by methods of statistical mechanics (8). But as the foregoing analysis has demonstrated, the constants \( g_f \) and \( g_r \) are composite in that they are net transmission factors which result from the summed effect of many processes, each separate one of which must be dynamically reversible.

The constant \( g_f \) fills the role assigned to \( \kappa_f \nu_f \) and \( g_r \) fills the role assigned to \( \kappa_r \nu_r \) of Eq. (7). In the more usual formulation of transition state theory, the transmission coefficients \( \kappa_f \) and \( \kappa_r \) give the fraction of activated complexes that successfully complete the transit over the full reaction path, while in the analysis described above, the net flux of complexes that successfully complete the transit of the reaction barrier is found by subtracting from the total flux across the barrier the flux of particles that are returned by any of the possible paths between reactants and products.
III. DISCUSSION

The analysis in this paper is based on acceptance of an underlying premise of transition state theory— that the rate of a forward or reverse reaction is determined by decomposition of an activated complex which is itself maintained at equilibrium with a set of reactants or products. The generality of the proof thus is dependent on the range of conditions over which transition state theory can be applied.

The equilibrium hypothesis of transition state theory is considered suitable only when the molar activation energy is greater than RT (16). Present (17) has shown that for bimolecular collision reactions in which the activation energies are 5RT, the equilibrium hypothesis for transition states leads to predicted rates of reaction that are too fast by the order of 8%. Furthermore, Prigogine and co-workers (18) have shown that the heat released in exothermic reactions can alter the activation rate from the expected equilibrium value.

It is apparent from experimental evidence, however, that in condensation reactions a near equilibrium distribution of transition state particles can be maintained despite sometimes low activation energies and despite the fact that condensation is always exothermic. Essentially all vapor molecules of certain chemical classes are condensed upon collision with a surface of the substance forming the vapor (2)(19). This means that there is a negligible thermal free energy barrier to condensation (2). The heating produced by condensation has no measurable effect on the reaction kinetics in the low pressure ranges usually studied, but would cause measurable surface heating at sufficiently high condensation fluxes. The reason that the equilibrium hypothesis is
valid for condensation over a broader range than for most other type of reactions are that under the usual conditions of study, a vapor of Maxwell-Boltzmann energy distribution is continuously provided and that the condensed phase provides a massive heat sink for the heat released by the reaction.

The arguments of the derivation show that when the equilibrium hypothesis can be accepted, Eq. (3) is valid for each separate path of a multiple-path reaction. The equation is also valid for each step in a reaction sequence for which two or more thermal free energy barriers are of comparable height. This conclusion is seen by considering the first intermediate product separated by the first barrier from the reactants to be reaction products and carrying through for that first barrier the kind of analysis that has been described and then by repeating the analysis for each successive barrier.

Application of the proof can be illustrated by its use in vaporization kinetics, the area which interested us in the questions discussed in this paper. As has been remarked, the proof is limited to demonstration of the relation between rate constants and equilibrium constants at fixed non-equilibrium conditions. These conditions of proof justify cancellation of the ratio $\alpha_c/\alpha_v$ which appears in the expression derived by Faule and Margrave (5) to relate apparent pressures to equilibrium pressures in effusion studies and also justifies replacement of a remaining term in $\alpha_c$ by $\alpha_v$. The form of the equation originally derived by Whitman (20) and Motzfeld (21) on the assumption that $\alpha_v = \alpha_c$ is then regained. But the value of $\alpha_v$ in an effusion cell may not be the same as that measured in free surface vaporization experiments since $\alpha_v$ might
vary with the pressure. In fact, one means of determining whether or not $\alpha_v$ is a function of pressure is to compare values of $\alpha_v$ calculated by means of the Whitman-Motzfeld equation with values calculated from free surface vaporization experiments.

Presently available experimental evidence suggests, however, that the assumption that $\alpha_v$ is independent of pressure is very satisfactory for many substances for steady state effusion from chambers maintained with pressures of the vapor between zero and the equilibrium pressure.

The equality between $\alpha_v$ and $\alpha_c$ that has been demonstrated for fixed reaction conditions shows that a model which assigns them different temperature dependences (6) is in that respect mistaken and in consequence likely to yield misleading conclusions. Transition state theory when applied (2)(3) to the various possible rate limiting steps identified in the terrace-ledge-kink-model (19) of vaporization and condensation appears at present to provide our most promising avenue to improved understanding of vaporization and condensation kinetics.

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4. A. W. Searcy and D. Beruto, to be published.


   evaluate an equilibrium constant in terms of thermal free energies
but use the less descriptive term excess free energy.


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