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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. One application of this proof is shown to be that vaporization and condensation coefficients must be equal for any specified non-equilibrium conditions.

I. Introduction

One of the most important questions of reaction kinetics is the cir-
cumstances under which the ratio of the rate constants for a forward and
reverse reaction can be equated to the equilibrium constant for the
reaction in question. The principle of microscopic reversibility[2]
requires the equality at equilibrium, and experimental verification of
the relationship to within reasonable error limits has been obtained for
particular reactions far from equilibrium.[3] But theoretical proof of
the relation apparently has been given only for ideal solutions.[4-6]
Furthermore, Johnston recently commented that those proofs are either
qualitative or are lacking in generality.[3]

Our attention was attracted to the problem of obtaining a more
general and quantitative proof when, in the course of adapting a model
for vaporization kinetics[7,8] to analysis of the kinetics of decomposition
reactions, two of us derived an expression for the effect of a porous
layer on the decomposition rate.[9] The expression depends on the conden-
sation coefficient α_c--that is, on the fraction of those molecules strik-
ing a surface that traverse any free energy barrier to the condensation
process.

The condensation coefficient is difficult to measure directly,
although the vaporization coefficient α_v--that is, the ratio of the
measured vapor flux from a surface to the maximum possible flux calcu-
lated from the Hertz-Knudsen-Langmuir equation—can readily be obtained
from experimental measurements of rates of vaporization in vacuum.[7,10]
By the principle of microscopic reversibility, the condensation co-
efficient 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[10] have warned against
assuming the equality $\alpha_v = \alpha_c$ in those effusion studies in which the
pressure is reduced below the equilibrium value. Ackermann, Thorn and
Winslow[11] 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 <u>under
fixed experimental conditions</u> the vaporization and condensation co-
efficients 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. Before discussing this
general question, which is the focus of our paper, we will review the
connection between vaporization coefficients, condensation coefficients,
and the rate constants for the vaporization and condensation processes.[12]

By definition $\alpha_v = J_v/J_{max}$ 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 success-
fully 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_{max} 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

$$J_s = \frac{P}{(2\pi MRT)^{1/2}} \tag{1}$$

where M is the molecular weight of the vapor molecule, R is the gas con-
stant and T is the absolute temperature. Equation (1) yields J_{max} when
the pressure is the equilibrium pressure P_e.

The equilibrium pressure is related to the standard free energy of
vaporization ΔG_v^o by

$$P_e = \exp\left(-\Delta G_v^o/RT\right) \tag{2}$$

Using standard formulations of reaction kinetics,[13,14] the vaporization rate,
if it is assumed to be governed by a single rate-limiting step that is
unaffected by catalysts or impurities, can be written as

$$J_v = \kappa_v \nu_v \exp\left(-\Delta G_v^*/RT\right) \tag{3}$$

where κ_v is the transmission coefficient, ν_v is the frequency factor
and ΔG_v^* is the free energy of activation for the vaporization process.

The rate of condensation is

$$J_c = \kappa_c \nu_c P \exp(-\Delta G_c^*/RT) \tag{4}$$

where the subscripts designate the condensation process. But by (1) and (2)

$$J_{max} = \frac{\exp(-\Delta G_v^O/RT)}{(2\pi MRT)^{1/2}} \tag{5}$$

and for α_v to be equal to α_c requires that the value of (3) divided by (5) be equal to (4) divided by (1), or that, when the common factor $(2\pi MRT)^{1/2}$ is eliminated

$$\frac{\kappa_v \nu_v \exp(-\Delta G_v^*/RT)}{\exp(-\Delta G_v^O/RT)} = \kappa_c \nu_c \exp(-\Delta G_c^*/RT). \tag{6}$$

If this relationship can be proved for non-equilibrium conditions, then the equality $\alpha_c = \alpha_v$ is proved for non-equilibrium conditions.

Equation (6) can be recognized as a special example of a general relation,

$$\frac{\kappa_f \nu_f \exp(-\Delta G_f^*/RT)}{\exp(-\Delta G_n^O/RT)} = \kappa_r \nu_r \exp(-\Delta G_r^*/RT) \tag{7}$$

where the subscript f indicates factors of the slow step of the forward reaction, r factors of the reverse reaction, and ΔG_n^O is the standard free energy of the overall reaction written in the forward direction. When (7) is written in terms of the rate constants $k_f = \kappa_f \nu_f \exp(-\Delta G_f^*/RT)$,

$$k_r = \kappa_r \nu_r \exp\left(-\frac{\Delta G^*}{RT}\right)$$ and the equilibrium constant $K_{eq} = \exp(-\Delta G_n^c/RT)$ for the reaction and rearranged (7) becomes

$$\frac{k_f}{k_r} = K_{eq} = \exp(-\Delta G_n^o/RT) \tag{8}$$

Rice[3] has proved Eq. (8) for some important non-equilibrium con-
ditions. His proof assumes that concentrations of reactants and products
remain small. In consequence, the reaction environment is held essen-
tially 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[5,6] considered by
means of his general analysis.

Rice's proof justifies use of Eq. (8), for example, for the analysis
of low pressure gas-phase reactions, but does not prove the equation when
the thermal, as distinct from configurational, portion of the free
energy[15] barrier to reaction may be different from the barrier under
equilibrium conditions. Surface morphology, and therefore the concen-
tration 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 free energy 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 the non-equilibrium conditions is the same or dif-
ferent from that under equilibrium conditions.

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 for the forward reaction has (1) a
thermal free energy (its free energy other than configurational free
energy of particle mixing)[15] equal to or greater than the saddle point
free energy barrier to reaction and (2) a trajectory directed past the
saddle point free energy barrier in the direction of 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 among the products and

possible catalysts and has an opposite trajectory from the complex pro-
duced from reactants.

It is assumed that both reactants and products of an elementary
step are capable of establishing independently an equilibrium distribu-
tion of states up to and including any state that can undergo a decompo-
sition that would be irreversible, or partly so, in the absence of an
equal or greater opposite flux from a second source. This kind of
assumption is customarily made in transition state theory for the for-
ward reaction studied far from equilibrium.[13,14]

Suppose the net reaction to be considered is

$$qA + rB = A_q B_r \tag{9}$$

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

$$mA + nB + pC \;\overset{\rightarrow}{\leftarrow}\; A_m B_n C_p^* \rightarrow A_q B_r + (m - q)A + (n - r)B + pC \tag{10}$$
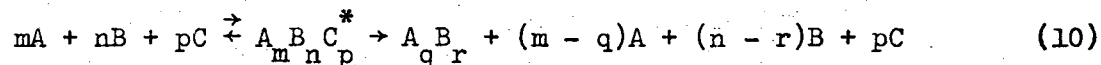
where $A_m B_n C_p^*$ is the activated complex for this reaction path. Any
reaction product in the system will establish an equilibrium distribu-
tion of accessible excited states and of products of reaction with matter
in the system environment, and some activated complexes will be formed
from the reaction product with trajectories which will carry these com-
plexes back across the saddle point free energy barrier.

The net rates of the forward and reverse reactions, J_f and J_r, can be written

$$J_f = \frac{d[X_{A_q B_r}]}{dt} = g_f \overset{f}{\underset{\rightarrow}{[X_{A_m B_n C_p}^*]}} \qquad (11)$$

$$J_r = - \frac{d[X_{A_q B_r}]}{dt} = g_r \overset{r}{\underset{\leftarrow}{[X_{A_m B_n C_p}^*]}} \qquad (12)$$

where $[X_{A_q B_r}], \overset{f}{\underset{\rightarrow}{[X_{A_m B_n C_p}^*]}}$ and $\overset{r}{\underset{\leftarrow}{[X_{A_m B_n C_p}^*]}}$ are the concentrations of the products and of activated complexes of the forward and reverse reactions, respectively, and g_r and g_f are proportionality constants to be evaluated later. The thermodynamic relations between reactants, products and activated complexes are illustrated in Fig. 1. Since the products and reactants are taken to be in equilibrium with their respective activated complexes, the free energy changes in the two vertical steps are zero and ΔG_a, the free energy difference between the activated complexes which are produced by equilibration with products and complexes produced by equilibration with reactants is equal to the free energy change of the overall reaction, ΔG_n. Complexes that differ only in having opposite trajectories across a free energy barrier must be identical in thermal free energy contents,[15] so the difference ΔG_a in free energies between complexes of the reverse and forward reaction directions depends only on their concentrations, that is

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

$$\frac{k_f}{k_r} = \exp\ (-\Delta G_n^O/RT)\ \frac{g_f}{g_r} \tag{13}$$

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 Σj_{ri}^O, and the reverse flux will be the sum of several components j_r, j'_f and Σj_{fi}^O, 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 Σj^O_{fi} 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

Σj^O_{ri} 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', Σf^O_i, r, r', and Σr^O_i 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

$$J_{ft} = f\,X^*_f + r'\,X^*_r + \sum_i r^O_i X^*_{ri} = rX^*_r + f'\,X^*_f + \sum_i f^O_i X^*_{fi} = J_{rt} \quad (14)$$

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 com-

plex in the reverse reaction. But, for example,

$$r^O_i X^*_{ri} = r''_i X^*_r \quad (15)$$

at equilibrium by the principle of microscopic reversibility, where r''_i

is the proportionality constant relating the flux of reactants crossing

the thermal free energy barrier at the point of interest and sub-

sequently 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

$$(f-f' - \sum_i f''_i)X^*_f = (r-r'' - \sum_i r''_i)X^*_r \tag{16}$$

At equilibrium $X^*_f = X^*_r$, and therefore the principle of microscopic reversibility requires also at equilibrium that

$$f-f' - \sum_i f''_i = r-r' - \sum_i r''_i \tag{17}$$

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 κ_f and κ_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 repeat-
ing the analysis for each successive barrier.

Application of the proof can be illustrated by its use in vaporiza-
tion kinetics, the area which interested us in the questions discussed
in this paper. As has been remarked, the proof is limited to demonstra-
tion of the relation between rate constants and equilibrium constants at
fixed non-equilibrium conditions. These conditions of proof justify
cancellation of the ratio α_c/α_v which appears in the expression derived
by Paule and Margrave (5) to relate apparent pressures to equilibrium
pressures in effusion studies and also justifies replacement of a remain-
ing term in α_c by α_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 α_v in an effusion cell may not be the same
as that measured in free surface vaporization experiments since α_v might

vary with the pressure. In fact, one means of determining whether or
not α_v is a function of pressure is to compare values of α_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 α_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 α_v and α_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 con-
sequence 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.

<div align="center">ACKNOWLEDGMENTS</div>

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