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# Reversible and irreversible formulation of unimolecular reactions

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A comparison is made between the reversible and irreversible formulations for a series of model isomerization reactions, and the conditions under which the differences are important are demonstrated.

In 1984, Quack<sup>1</sup> called attention to the apparent inconsistency between the reversible and irreversible descriptions of unimolecular reactions, using a model isomerization reaction as an example. He demonstrated with his model that the falloff of the unimolecular reaction rate is not due to a reduced population of the reactive levels—as we have accepted since the inception of unimolecular reaction theory in the 1920s—but rather due to a fast reverse reaction, caused by an overpopulation of *product* reactive levels which have not yet been deactivated to stable product; the reduction in population of the *reactant* reactive levels is only a minor contributor to the falloff in rate.

This observation raises the important question as to why the irreversible formulation of the unimolecular reaction rate, originally as a steady-state expression,<sup>2</sup> and more recently as the eigenvalue of an appropriate master equation,<sup>3</sup> can have been so successful. Presumably, the experiments performed so far have not been such as to reveal the discrepancies between the two approaches, and there is therefore a need to explore under what conditions these discrepancies will become apparent. The discussion of reversibility in chemical reaction-rate theory has a long history, with key references being Rice,<sup>4</sup> Pyun and Ross,<sup>5</sup> Snider,<sup>6</sup> Widom,<sup>7</sup> Lin and Laidler,<sup>8</sup> and Boyd.<sup>9</sup> Here, we will concentrate only on the issue raised by Quack,<sup>1</sup> in respect of unimolecular isomerization reactions, but extension to unimolecular dissociation reactions will be reasonably similar—very rapid equilibration between reactant states and reactive product levels, prior to deactivation to stable product, is already well established in recombination reactions.<sup>10</sup>

## REVERSIBLE AND IRREVERSIBLE RATE LAWS

Consider the reversible reaction between species  $R$  and  $P$ ,



where  $R$  and  $P$  are structureless entities; thus, the rate constants  $k_f$  and  $k_b$  are truly time independent, and the relaxation from any initial state with concentrations  $R(0)$ ,  $P(0)$  to equilibrium is given by

$$\Delta R(t) = \Delta R(0)e^{-\lambda_1 t}, \quad (1)$$

where  $\Delta R(t) = [R(t) - R_{eq}]$ ,  $R(t)$  being the concentration of  $R$  at time  $t$ ,  $R_{eq}$  being the equilibrium concentration of  $R$ , and  $\lambda_1 = (k_f + k_b)$ . Solving for  $\lambda_1$  gives

$$\lambda_1 = -\frac{d}{dt} \ln \left[ \frac{\Delta R(t)}{\Delta R(0)} \right]. \quad (2)$$

These equations could equally well have been written in terms of  $P$  instead of  $R$ .

If we assume, as for example in a radioactive decay, that  $R_{eq} = 0$ , then, formally, Eq. (2) still holds, but  $\Delta R = R$ , viz.,

$$\lambda_1 = -\frac{d}{dt} \ln \left[ \frac{R(t)}{R(0)} \right]. \quad (2a)$$

The only difference is that the population  $R(t)$  shrinks exponentially to zero with rate constant  $\lambda_1$ , whereas in the reversible case, it is the difference  $[R(t) - R_{eq}]$  that does so; also, when  $R_{eq} = 0$ , the equilibrium constant  $K_{eq} = P_{eq}/R_{eq} = \infty$ ,  $k_b = 0$ , and  $\lambda_1 = k_f$ .

The question, therefore, is to what extent the unimolecular reactions that have been studied in the past could be interpreted properly on the assumption that  $K_{eq} \gg 1$ ,  $k_b \ll k_f$  and, therefore,  $\lambda_1 = k_f$ , whence the distinction between Eqs. (2) and (2a) would be irrelevant?

## THE TIME-DEPENDENT RELAXATION COEFFICIENT

If we now consider a real case where  $P$  and  $R$  have many states, not all of which are reactive, the right-hand side of Eq. (2) is no longer time independent;  $K_{eq}$  is also considered to be finite and, of course, for an isomerization, it does not vary with pressure. Following Quack,<sup>1</sup> we define a relaxation coefficient  $k_r(t)$  as

$$k_r(t) = -\frac{d}{dt} \ln \left[ \frac{\Delta R(t)}{\Delta R(0)} \right], \quad (3)$$

which has the property that after all the transients have died out, it approaches the limiting value  $\lambda_1$ , viz.,

$$\lambda_1 = \lim_{t \rightarrow \infty} \left\{ -\frac{d}{dt} \ln \left[ \frac{\Delta R(t)}{\Delta R(0)} \right] \right\}. \quad (4)$$

We can express  $k_r(t)$  in Eq. (3) in terms of the individual deviations of the reactant and product states from their equilibrium values.

Let the concentrations of the reactant states be  $\{R_0, R_1, \dots, R_n\}$ ,  $R = \sum_{i=0}^n R_i$ , with decay rate constants to product  $P$  of  $\{d_0, d_1, \dots, d_n\}$ ; likewise, for the product states,  $\{P_0, P_1, \dots, P_m\}$ ,  $P = \sum_{j=0}^m P_j$ , with decay rate constants to reactant  $R$  of  $\{d'_0, d'_1, \dots, d'_m\}$ ; many of the  $d_i$ ,  $d'_j$  of low index will be zero, corresponding to nonreactive states below threshold; also,  $(m + n + 2) = (N + 1)$ , the total number of reactant and product states combined. We have

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$$\begin{aligned} \frac{d}{dt} \ln \left[ \frac{\Delta R(t)}{\Delta R(0)} \right] &= \frac{d}{dt} \ln \Delta R(t) = \frac{1}{\Delta R} \frac{dR}{dt} = \frac{1}{\Delta R} \frac{d}{dt} \left( \sum_{i=0}^n R_i \right) \\ &= \frac{1}{\Delta R} \left( - \sum_{i=0}^n d_i R_i + \sum_{j=0}^m d'_j P_j \right). \end{aligned} \quad (5)$$

The appearance of Eq. (5) can be improved by writing  $\Delta P = -\Delta R$ , whence

$$k_r(t) = \sum_{i=0}^n d_i \left( \frac{R_i}{\Delta R} \right) + \sum_{j=0}^m d'_j \left( \frac{P_j}{\Delta P} \right). \quad (6)$$

The addition of

$$0 = - \sum_{i=0}^n d_i \left( \frac{R_i^{\text{eq}}}{\Delta R} \right) + \sum_{j=0}^m d'_j \left( \frac{R_j^{\text{eq}}}{\Delta R} \right)$$

gives

$$\begin{aligned} k_r(t) &= \sum_{i=0}^n d_i \left( \frac{R_i}{\Delta R} \right) - \sum_{i=0}^n d_i \left( \frac{R_i^{\text{eq}}}{\Delta R} \right) \\ &\quad + \sum_{j=0}^m d'_j \left( \frac{P_j}{\Delta P} \right) + \sum_{j=0}^m d'_j \left( \frac{R_j^{\text{eq}}}{\Delta R} \right) \\ &= \sum_{i=0}^n d_i \left[ \frac{(R_i - R_i^{\text{eq}})}{\Delta R} \right] + \sum_{j=0}^m d'_j \left[ \frac{(P_j - P_j^{\text{eq}})}{\Delta P} \right]. \end{aligned} \quad (7)$$

We have made use of the detailed balancing relationship

$$\sum_{i=0}^n d_i \left( \frac{R_i^{\text{eq}}}{\Delta R} \right) = \sum_{j=0}^m d'_j \left( \frac{P_j^{\text{eq}}}{\Delta R} \right) = - \sum_{j=0}^m d'_j \left( \frac{P_j^{\text{eq}}}{\Delta P} \right)$$

in order to set Eq. (7) into this symmetric form. Finally, writing  $\Delta R_i = (R_i - R_i^{\text{eq}})$ , we can simplify Eq. (7) to

$$k_r(t) = \sum_{i=0}^n d_i \left( \frac{\Delta R_i}{\Delta R} \right) + \sum_{j=0}^m d'_j \left( \frac{\Delta P_j}{\Delta P} \right). \quad (8)$$

## FLUX COEFFICIENTS

Equation (8) is the key to understanding the kinetic behavior of reversible isomerization with internal structure; it expresses Quack's relaxation coefficient in terms of the departure of each reactive flux from its equilibrium value, weighted according to the departure of the total species concentration from its equilibrium value. Equation (8) does not diverge as the system approaches equilibrium, since  $\sum_{i=0}^n \Delta R_i = \Delta R$ , likewise for  $\Delta P$ . Notice also that for the structureless case, in which both  $R$  and  $P$  each only have one reactive level,  $k_r(t)$  becomes  $(d_0 + d'_0)$ , i.e.,  $(k_f + k_b)$  in the usual nomenclature.

For the irreversible case, i.e.,  $R_i^{\text{eq}} = 0$ ,  $\Delta R_i = R_i$ , then

$$\begin{aligned} k_r(t) &= \sum_{i=0}^n d_i \left( \frac{\Delta R_i}{\Delta R} \right) \\ &= \sum_{i=0}^n d_i \left( \frac{R_i}{R} \right) = \sum_{i=0}^n d_i n_i = r(t). \end{aligned} \quad (9)$$

Here,  $n_i$  is the instantaneous fractional population of state  $i$ , in the usual nomenclature,<sup>3</sup> and  $r(t)$  is the forward flux per unit of concentration, i.e., the flux coefficient;<sup>7</sup> likewise, we

can define  $r'(t)$  for the reverse reaction proceeding under irreversible conditions.

## RELATIONSHIPS BETWEEN RATE AND FLUX COEFFICIENTS

We can write for the rate of disappearance of  $R$ ,

$$\begin{aligned} - \frac{dR}{dt} &= \sum_{i=0}^n d_i R_i - \sum_{j=0}^m d'_j P_j \\ &= \sum_{i=0}^n d_i \left( \frac{R_i}{R} \right) R - \sum_{j=0}^m d'_j \left( \frac{P_j}{P} \right) P \\ &= r(t)R - r'(t)P, \end{aligned} \quad (10)$$

and, as is well known, the formal similarity with the phenomenological rate equation

$$- \frac{dR}{dt} = k_f R - k_b P$$

is misleading, because although  $k_f/k_b = K_{\text{eq}}$ ,  $K(t) = r(t)/r'(t) < K_{\text{eq}}$ , except in the limits of time and pressure  $\rightarrow \infty$ .

Simple manipulation of either Eq. (8) or (10) yields the connection between the relaxation coefficient and the flux coefficients, i.e.,

$$k_r(t) = \frac{R}{\Delta R} r(t) + \frac{P}{\Delta P} r'(t) \quad (11)$$

If we now make use of the conservation condition that  $(R + P) = \text{const} = R_0$ , say, and remembering that  $\Delta R = -\Delta P$ , Eq. (11) becomes

$$k_r(t) = \frac{R}{\Delta R} [r(t) + r'(t)] - \frac{R_0}{\Delta R} r'(t), \quad (12)$$

one of the many ways in which this relationship can be expressed; other useful forms include the difference between the equilibrium constant  $K_{\text{eq}}$  and the instantaneous value of  $K(t)$ , the ratio of the forward and reverse flux coefficients.

In the irreversible case,  $r'(t) = 0$ ,  $K_{\text{eq}} = \infty$ , and  $K(t) = \infty$ , hence

$$k_r(t) \rightarrow \frac{R}{\Delta R} r(t) = r(t),$$

since  $R/\Delta R = 1$ . The long-time limit of  $k_r(t)$  is  $\lambda_1$  and of  $r(t)$  is  $\gamma_0$ , the eigenvalue corresponding to the rate constant for the irreversible case (see below); thus, as the irreversible limit is approached,  $\lambda_1 \rightarrow \gamma_0$ .

## ILLUSTRATIVE MODEL

In Fig. 1, we depict four possible models with which to illustrate the properties of a unimolecular isomerization reaction. Model (i) is the usual irreversible one, whose properties are well known.<sup>3</sup> Model (ii) is a simple reversible one in which, once the forward reaction-rate constants  $d_i$  are given, the reverse reaction-rate constants  $d'_j$  are determined by detailed balancing, thus ensuring that  $k_f/k_b = K_{\text{eq}}$ . In model (iii), all of the product states are lumped into a single structureless entity, with the reverse rate constants, now labeled  $d''_j$ , still determined by detailed balancing; as we shall see, this model is instructive because it lacks some essential features. Finally, in model (iv), the states above threshold are

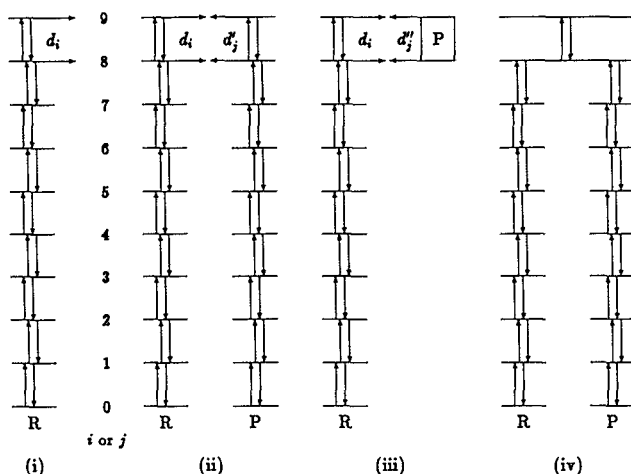


FIG. 1. Schematic representation of four possible models for illustrating the properties of unimolecular isomerization reactions: (i) irreversible; (ii) reversible; (iii) reversible, with a single lumped-product state; (iv) reversible, with common connecting states.

regarded as being common to both molecular species as, for example, one might find in a free rotation above a torsional barrier; however, it is clear that if there is no time delay between the states of  $R$  and the states of  $P$ , the reaction will always be first order in pressure, and cannot exhibit unimolecular behavior.

For the purposes of illustration, we choose these models to be very simple: 10 states in each manifold, two above and eight below threshold; Landau-Teller transition probabilities between adjacent states, with different magnitudes in each manifold to avoid complicating resonances, and connection via  $d$  and  $d'$  only between like-numbered states in each manifold. Increasing the number of states, increasing the connectivity between the states in each manifold, or increasing the connectivity between the two manifolds only affects the fine details but not the patterns of behavior of the normal modes of relaxation. The eigenvalues which correspond to the unimolecular rate of reaction for each of the three models will be designated as irreversible model (i),  $\gamma_0$ ; reversible model (ii),  $\lambda_1$ ; reversible, lumped-product model (iii),  $\bar{\lambda}_1$ . Figure 2 shows the behavior of these three quantities as a function of pressure for a system in which the equilibrium constant  $K_{eq} = 10$ ; the larger the equilibrium constant, the smaller the differences between these curves. In this diagram,  $\bar{\lambda}_1$  for the lumped-product model is shown as a dashed line because it is only of minor importance. It can be seen that, except at one point where they cross,  $\gamma_0$  and  $\lambda_1$  are never the same. At the high-pressure limit,  $\lambda_1 > \gamma_0$  and, in fact, as is well known,  $\lambda_1 = \bar{\lambda}_1 = \gamma_0(1 + K_{eq})/K_{eq}$ . On the other hand, there is no such simple relationship at the low-pressure limit where  $\lambda_1 < \gamma_0 < \bar{\lambda}_1$ .

## POPULATION DISTRIBUTIONS

Before we can discuss these differences, it is necessary to examine the population distributions in the steady regimes for which these rate constants have meaning. Figure 3 shows

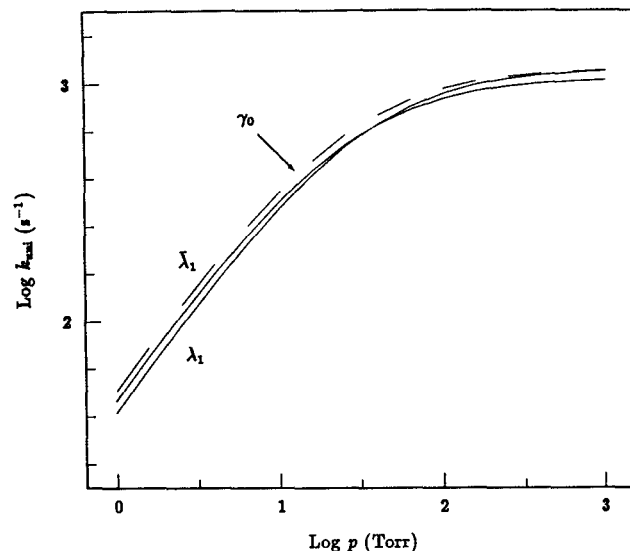


FIG. 2. Plot of the eigenvalues, as a function of pressure, given by three of the models:  $\gamma_0$  for irreversible model (i);  $\lambda_1$  for reversible model (ii);  $\bar{\lambda}_1$  for lumped-product reversible model (iii);  $\gamma_0$  and  $\lambda_1$  are shown as solid lines,  $\bar{\lambda}_1$  as a dashed line. This calculation is for the case of  $K_{eq} = 10$ .

the model (ii) populations of reactant and product states for the process  $R \rightarrow P$  in the steady regime, i.e.,  $t \gg 1/\lambda_1$ , for the case of  $K_{eq} = 10$  at low pressure. It can be seen that the relative extent of overpopulation of the states  $R_i$  declines

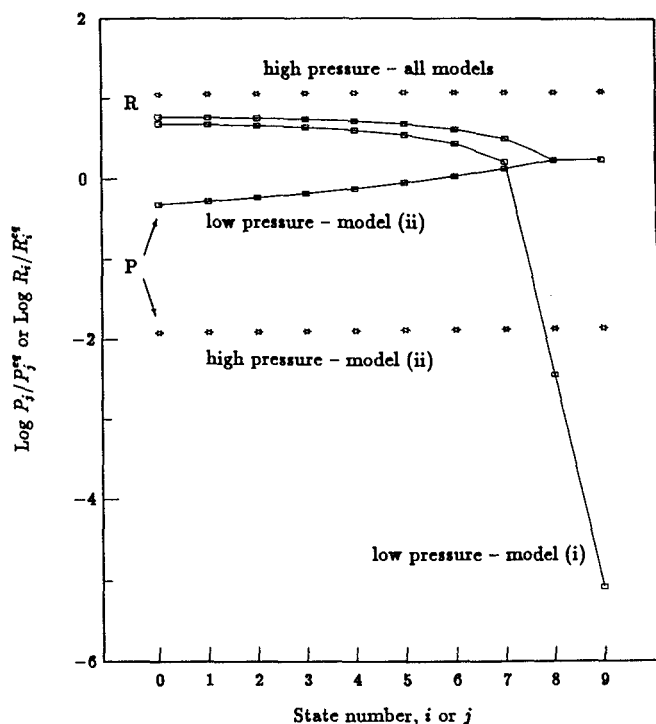


FIG. 3. Plots of populations, relative to their final equilibrium values, for the reversible reaction  $R \rightarrow P$ ,  $K_{eq} = 10$ , at a time  $t \gg 1/\lambda_1$ : solid lines, reversible model (ii) at low pressure; also, irreversible model (i) at same time and pressure; points, reversible model (ii) at high pressure; populations of  $R$  for the irreversible model (i) at high pressure are indistinguishable from those for the reversible model.

with increasing  $i$  throughout the unreactive region but, nevertheless, all states of  $R$  are overpopulated, including the reactive states; contrast this with the corresponding irreversible result, model (i), where the reactive states are hugely underpopulated. Now looking at the product states, the reactive ones are virtually in equilibrium with the corresponding reactant states, as is expected because the rate constants  $d_i, d'_j$  connecting them are large compared with the activation and deactivation rates in the low-pressure regime. In this example, one of the bound states of the product  $P$  is also slightly overpopulated, but the relative degree of underpopulation of the remaining product states increases as the index  $j$  decreases.

Also shown in Fig. 3, simply as points, are the populations of these states at a pressure near the first-order limit; both sets of points are almost horizontal but, in fact, the top one slopes downwards with increasing  $i$ , and the lower one slopes slightly upwards with increasing  $j$ . The reactive states are no longer in equilibrium with each other because, now, the  $d_i, d'_j$  are small relative to the collisional relaxation rates; this separation starts to take place as the rate law starts to depart from second order, beginning with those states whose interconversion rates are the smallest, and progressing through the more rapidly reacting states as the pressure rises. Also, the larger the equilibrium constant  $K_{eq}$ , the more quickly does this separation occur, and the more nearly does the population distribution for the reversible model approach that given by the irreversible one.

If the reaction is started in the opposite direction, i.e.,  $P \rightarrow R$ , then the population distributions in the steady regime are just the mirror images of those shown for the reversible case in Fig. 3, e.g., at low pressure, the first seven states of  $P$ , i.e.,  $0 < j < 6$ , are overpopulated and all states of  $R$  are underpopulated. In fact, there is a direct connection between the degree of overpopulation of a state when the reaction is proceeding in one direction and its degree of underpopulation when it is proceeding in the opposite direction. We can see this by inspecting the normal-mode equations describing the relaxation. We begin with Eq. (2.17) of Ref. 3, which gives the population  $n_i(t)$  of state  $i$  at time  $t$  in terms of the equilibrium population  $\tilde{n}_i$  of that state, the appropriate set of normal modes and fluxes, and the relaxation eigenvalues  $\lambda_j$ , viz.,

$$n_i(t) = \tilde{n}_i + \sum_{j \neq 0} (\Omega_j)_i e^{-\lambda_j t}. \quad (13)$$

In this equation

$$(\Omega_j)_i = (S_0)_i (S_j)_i \times (S_j, E^{-1/2} \mathbf{n}(0)), \quad (14)$$

where  $S_j$  is the eigenvector of the symmetrized relaxation matrix corresponding to eigenvalue  $\lambda_j$ ;  $E^{-1/2}$  is one of a pair of diagonal matrices which are used to symmetrize the original relaxation matrix, with elements  $E_{ii}^{-1/2} = \tilde{n}_i^{-1/2}$ ;  $\mathbf{n}(0)$  is the initial population distribution at time  $t = 0$ , and  $(,)$  denotes the scalar product of two vectors; finally,  $S_0$ , the eigenvector corresponding to  $\lambda_0 = 0$  has elements  $(S_0)_i = \tilde{n}_i^{1/2}$ . The significance of the terms in Eq. (14) is that the product  $(S_0)_i (S_j)_i = (M_j)_i$  is the  $i$ th component of the normal mode of relaxation  $M_j$ , and the scalar product

term represents the flux using that mode to achieve the required equilibrium distribution; see Ref. 3 for further details.

In the long-time regime, only terms in  $\lambda_1$  remain, giving

$$n_i(t) = \tilde{n}_i + (S_0)_i (S_1)_i \times (S_1, E^{-1/2} \mathbf{n}(0)) e^{-\lambda_1 t}. \quad (15)$$

If the starting distribution  $\mathbf{n}(0)$  happens to be the equilibrium distribution, then the product  $E^{-1/2} \mathbf{n}(0)$  is the vector  $S_0$ , and the scalar product  $(S_1, S_0) = 0$  because all the eigenvectors of the relaxation matrix are orthogonal; hence there is no flux. For any other starting distribution, the flux term is nonzero: we will just consider two idealized cases, one where the starting vector is  $\mathbf{n}(0) = \{1, 0, \dots, 0\}$  (all molecules in the ground state of  $R$ ), and  $\mathbf{n}(0) = \{0, \dots, 0, 1\}$  (all molecules in the ground state of  $P$ ); evaluating the scalar product in Eq. (15), the flux terms become  $(S_1)_0 (S_0)_0$  and  $(S_1)_N (S_0)_N$  respectively.

At the very high pressures,  $M_1$  is simply a normal mode which transfers molecules from states of  $R$  into states of  $P$ , and *vice versa*, with rate constant  $\lambda_1$ ; thus, all the eigenvector elements of  $S_1$  corresponding to states of  $R$  have one sign, and those corresponding to states of  $P$ , the other. For the reaction in the forward direction, choose  $(S_1)_0$  to be positive, making the term  $(S_1)_0 (S_0)_0$  positive: then, for all  $i$  corresponding to  $R$  in Eq. (15) the second term is positive, and for those corresponding to  $P$ , it is negative; thus, the individual populations of  $R$  fall towards their equilibrium values, and those of  $P$  rise, as expected. If the reaction goes in the opposite direction, then with the same choice of signs, the flux term  $(S_1)_N (S_0)_N$  is negative: now, the second term in Eq. (15) is positive for states of  $P$  and negative for states of  $R$ , as required.

At the low pressures, the  $d_i, d'_j$  are no longer insignificant relative to the relaxation rates, and the sign change in  $S_1$  no longer corresponds exactly with the projection of the states onto those of  $R$  and  $P$ ; in the example shown in Fig. 3, the sign change occurs between the seventh and eighth states of  $P$  (i.e., between  $j = 6$  and  $7$ ).

### THE RELATIVE MAGNITUDES OF $\lambda_1, \gamma_0$ , AND $\bar{\lambda}_1$

We first examine the makeup of the quantity  $k_r(t)$ , whose long-time limit is  $\lambda_1$ ; we make use of Eq. (8), and in Fig. 4, we plot the behavior of its two components for the case of  $R \rightarrow P$ ,  $K_{eq} = 10$ , at very low pressure. The factors

$$q = \sum_{i=0}^n d_i \left( \frac{\Delta R_i}{\Delta R} \right) \quad \text{and} \quad q' = \sum_{j=0}^m d'_j \left( \frac{\Delta P_j}{\Delta P} \right)$$

are really flux coefficients too, but Widom<sup>7</sup> has already used that term for the quantities  $r$  and  $r'$ ; to avoid confusion, we will refer to  $q$  and  $q'$  as generalized flux coefficients which, of course, reduce to  $\dot{r}$  and  $\dot{r}'$  as  $K_{eq} \rightarrow \infty$ .

At early times,  $q$  and  $q'$  depend upon the starting conditions: Here we have chosen all the molecules in the zeroth state of  $R$  (solid lines) and all states of  $R$  at equilibrium (dashed lines); the respective curves coalesce after the induction period. When the starting vector is  $\{1, 0, \dots, 0\}$ , all of the  $\Delta R_i$  for  $d_i \neq 0$  are negative, and so  $q$  is negative; on the other hand, when the starting distribution is the equilibrium for  $R$  only, all the  $\Delta R_i$  are positive, and so  $q$  is positive. Since in this example (see Fig. 3), the  $\Delta R_i$  remain positive,  $q$  con-

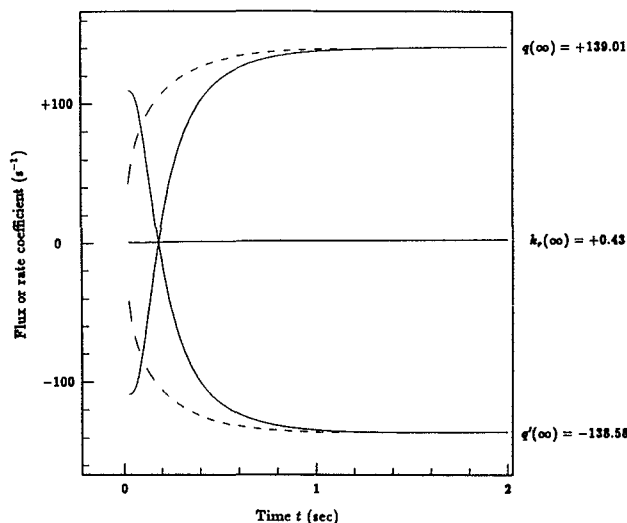


FIG. 4. Plots of the generalized flux coefficients  $q = \sum_{i=0}^n d_i (\Delta R_i / \Delta R)$  and  $q' = \sum_{j=0}^m d'_j (\Delta P_j / \Delta P)$  as a function of time for the reaction  $R \rightarrow P$ ,  $K_{eq} = 10$ , at very low pressure ( $10^{-2}$  Torr): solid lines, starting with all molecules in the lowest state of  $R$ ; dashed lines, starting with all states of  $R$  in thermal equilibrium. Notice the slight difference between the two  $k_r(t)$  at very early times.

tinues to be positive throughout the steady regime.

At these very low pressures, it can be seen that  $q$  and  $q'$  are virtually mirror images of each other. Concentrating on the steady regime, we can see from Fig. 3 that, for example, the  $\Delta R_i = (R_i - R_i^{eq})$  and the  $\Delta P_j = (P_j - P_j^{eq})$  are all positive for the reactive states [which are the only ones which contribute directly to  $k_r(t)$ ]; moreover, since the  $P_j^{eq} \sim 10P_i^{eq}$ , the  $\Delta P_j$  are numerically about 10 times as large as the  $\Delta R_i$ , but this is more-or-less offset by the fact that the  $d_i \sim 10d'_j$ . Thus,  $q$  and  $q'$  are approximately of equal numeri-

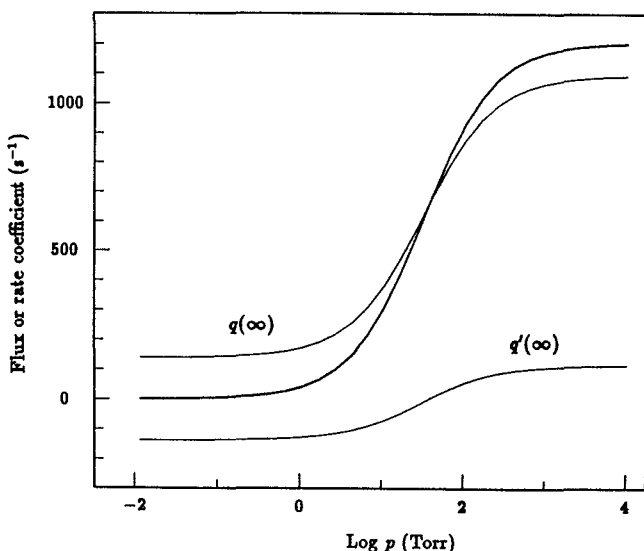


FIG. 5. Plot of variation of the steady values of the generalized flux coefficients as a function of pressure, for  $R \rightarrow P$ ,  $K_{eq} = 10$ ; the thick line represents the sum of  $(q + q') = k_r(\infty)$ .

cal magnitude, but have opposite signs since  $\Delta P = -\Delta R$ , and therefore  $\lambda_1$ , which (in the limit) is the sum of the two, has a very small value.

With increasing pressure, the symmetry between  $q$  and  $q'$  is lost, as is shown in Fig. 5:  $q$  increases with pressure from one limiting value to another;  $q'$  also changes from one limit to another over the same pressure range, but it also changes from negative to positive. The reason why  $q'$  is positive at high pressures is because (see Fig. 3) all the  $\Delta P_j = (P_j - P_j^{eq})$  are now negative which, in turn, is because the reactive states of  $P$  are deactivated by collision faster than they can be formed by reaction from  $R$ . At the crossover point, we have the condition that some  $\Delta P_j$  are positive and some are negative, i.e., some reactive product states are overpopulated and some are underpopulated, causing  $q'$  to become zero, and  $\lambda_1 = q$ .

It is not difficult to see why  $\lambda_1$  for the lumped-product model is always greater than  $\lambda_1$  for the fully reversible model. Since  $\Delta P_j$  and  $\Delta P$  are really the same thing for the lumped-product model, all the  $\Delta P_j / \Delta P = 1$ ; thus, Eq. (8) becomes

$$k_r(t) = \sum_{i=0}^n d_i \left( \frac{\Delta R_i}{\Delta R} \right) + \sum_{j=0}^m d'_j, \quad (16)$$

where  $d'_j = d'_j(P_j^{eq}/P_{eq})$ . For the reaction  $R \rightarrow P$ , and at any pressure, the populations of the states of  $R$  are very nearly the same for either model (ii) or model (iii); hence, the first terms in Eqs. (8) and (16) are virtually the same, and the difference must arise from a difference in the second terms. The second term in Eq. (16) is

$$\sum_{j=0}^m d'_j = \sum_{j=0}^m d'_j \frac{P_j^{eq}}{P_{eq}} = r'(\infty).$$

For the reaction  $R \rightarrow P$  at the low-pressure limit,  $q'$ , the second term in Eq. (8) is negative (see Fig. 3) and so the result of Eq. (16) is greater than that of Eq. (8). At higher pressures,  $q'$  is now positive, but because (Fig. 3 again) the fractional depopulation of the lower states is more severe than that of the upper states,  $(\Delta P_j / \Delta P) < (P_j^{eq} / P_{eq})$  and, again, the result of Eq. (16) is greater than that of Eq. (8). They become identical as  $P \rightarrow \infty$ , since then  $(\Delta P_j / \Delta P)$  and  $(P_j^{eq} / P_{eq})$  become the same thing. The possible existence of a bottleneck does not invalidate these conclusions: If the bottleneck is in the deactivation of  $P$ , then the higher states of  $P$  will be overpopulated, making  $q'$  negative, and will remain so up to higher pressures than if there were no bottleneck; on the other hand, if the bottleneck is in the activation of  $R$ , the states of  $P$  will be in close equilibrium with each other at lower pressures than otherwise would be the case, but the relative behavior of  $(\Delta P_j / \Delta P)$  and  $(P_j^{eq} / P_{eq})$  will still follow the same patterns, only with a shift to lower pressures.

What the lumped-product model lacks is the time delay between the formation of reactive product states and unreactive product states; no lumped-product model will be able to mimic the correct behavior unless the lumped state is far enough below threshold so that this delay is properly approximated in the calculation.

It is also easy to see why  $\lambda_1 > \gamma_0$  at the high-pressure

limit. Not shown in Fig. 3 are the populations of  $R$  at high pressure for the irreversible model, because they are indistinguishable from those for the reversible model. Thus, the first term in Eq. (8) is the same, but the second term is absent, ensuring that  $\lambda_1 > \gamma_0$ . At the low-pressure limit, it is not quite so simple. In the irreversible case, the second term in Eq. (8), which is normally negative at low pressures, is missing, so that  $\gamma_0$  would be expected to be greater than  $\lambda_1$ , as is found. However, the cancellation between the two terms in Eq. (8) is very close (see Fig. 4), and simply to remove the second term would cause  $\gamma_0 \gg \lambda_1$ , which is not true. This is because, in fact, at the low-pressure limit, the rate does not depend on the dissociation rates in either model. For the irreversible case, it is determined by the network properties among the unreactive states of  $R$ , and the rate at which crossings, caused by collision, to the reactive states take place.<sup>11</sup> In the reversible case, since the reactive states of  $R$  and  $P$  are always in equilibrium, the rate is determined co-operatively by the network properties of both manifolds of unreactive states. Some further analysis of this problem is required, in order to account for the relatively small difference between  $\gamma_0$  and  $\lambda_1$  at the low-pressure limit.

So far, we have concentrated on the differences between two theoretically meaningful relaxation rates  $\lambda_1$  and  $\gamma_0$ , but  $\lambda_1$  is not usually what is measured in a kinetic experiment. The usual forward rate constant is

$$k_f = \lambda_1 \left( \frac{K_{eq}}{1 + K_{eq}} \right), \quad (17)$$

and in Fig. 6, we show the relative magnitudes of the discrepancy between  $k_f$  and  $\gamma_0$  for various values of the equilibrium constant, all other parameters being kept constant. It can be seen that  $\gamma_0$  and  $k_f$  agree at the high-pressure limit, but that at the low-pressure limit,  $\gamma_0$  can exceed  $k_f$  by as much as about a factor of 3 or 4 for an isomerization when  $K_{eq} = 1$ ; by the time  $K_{eq}$  reaches 1000, the discrepancy is negligible.

## INDUCTION TIMES

Induction times have not yet played very much of a role in the study of unimolecular reactions,<sup>3</sup> but there are two points which should be noted for future reference. One is that all of our analysis refers to the steady regime which obtains once the induction period is complete, and the other is that the theoretical formulas by which induction times are calculated always contain  $\gamma_0$  or  $\lambda_1$  which, as we have seen, never agree. Determination of the induction time by extrapolating back the product concentration is, of course, unambiguous provided that there is a large separation between  $\lambda_1$  and the other eigenvalues corresponding to the internal relaxations.

Induction times depend upon the starting distribution, as is shown in the formulas below, and can be positive, zero, or negative;<sup>12</sup> again, for our simple discussion, we will assume that the starting distributions are either  $\{1, 0, \dots, 0\}$  (all  $R$  in its ground state) or  $\{0, \dots, 0, 1\}$  (all  $P$  in its ground state).

The formulas for the induction time in the irreversible model (i) have been given in many places;<sup>3</sup> here, for consistency, we will use the variant in which the eigenvectors  $\Psi_i$  of

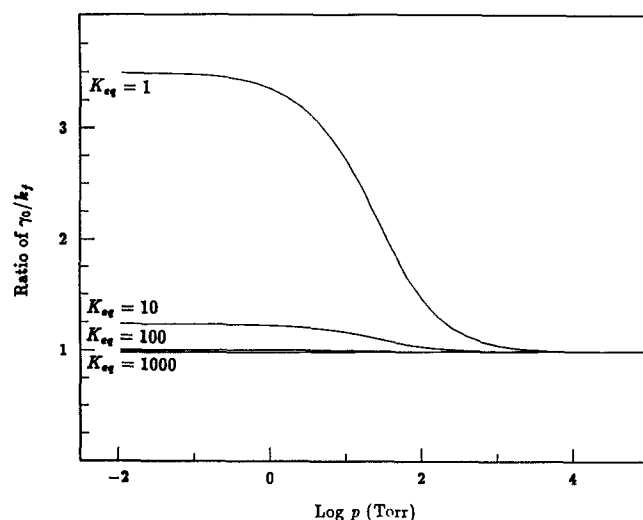


FIG. 6. Relative magnitudes of the discrepancy between  $\gamma_0$  and  $k_f$  for various values of the equilibrium constant for the model reactions (i) and (ii).

the symmetrized reaction matrix are normalized to unity in the normal manner, viz.,

$$\tau_{ind}^{irrev} = \gamma_0^{-1} \ln [ (S_0, \Psi_0) (\Psi_0, E^{-1/2} \mathbf{n}(0)) ]. \quad (18)$$

An analogous formula for the lumped-product model (iii) has been given,<sup>13</sup> and that for the fully reversible model (ii) is easily derived, viz.,

$$\tau_{ind}^{rev} = \lambda_1^{-1} \ln [ (S'_0, S'_1) (S_1, E^{-1/2} \mathbf{n}(0)) / (S'_0, S'_0) ], \quad (19)$$

where the prime denotes that the full vector is truncated by removal of elements corresponding to the reactant states. Equations (18) and (19) give the same result at high pressure, but they differ at low pressures by a factor of roughly

$$\tau_{ind}^{irrev} \sim \tau_{ind}^{rev} \left( \frac{K_{eq}}{1 + K_{eq}} \right)^2.$$

The reversible reaction achieves the steady condition more quickly than does the irreversible one; these differences will need further examination at a later date.

In the models which we have examined, the relaxation times for  $R$  and  $P$  were always different, and could be made quite different; thus, the induction times for  $R \rightarrow P$  and for  $P \rightarrow R$  could also be quite different, although this will not likely occur in practice, since in an isomerization, the vibrational properties of reactant and product will usually be rather similar. This difference arises because induction times are determined principally by the vibrational relaxation time corresponding to the given initial distribution. Whether the induction time is greater than or less than the vibrational relaxation time depends upon the nature of the relaxation matrix, and is not a topic to be pursued here. Notice that this correlation between induction and relaxation time is an indirect one, since neither the vector nor the eigenvalue corresponding to the vibrational relaxation appears in either Eq. (18), i.e.,  $\Psi_1$ , or Eq. (19), i.e.,  $S_2$  and/or  $S_3$ . In the reversible model, barring accidental interferences, there are usually two eigenvalues  $\lambda_2$  and  $\lambda_3$  which correlate, one with the rate of the  $1 \rightarrow 0$  transition in  $R$ , and the other in  $P$ ; let us say  $\lambda_2$

with the relaxation of  $R$  and  $\lambda_3$  with the relaxation of  $P$ . This information becomes incorporated into Eq. (19) through the flux term  $(S_1, E^{-1/2}n(0))$  since for the reaction  $R \rightarrow P$ , this picks up the zeroth element of  $S_1$ , whose magnitude is perturbed most strongly by  $\lambda_2$ , and for  $P \rightarrow R$ , it picks up the  $N$ th element of  $S_1$ , whose magnitude is perturbed most strongly by  $\lambda_3$ .

Referring back to Fig. 4, it is seen that the forward and the reverse generalized flux coefficients ( $q$  and  $q'$ ) approach their steady value on the same time scale which, in this case, correlates with  $\lambda_2$ ; for the reverse reaction  $P \rightarrow R$ , the time scale would be different if  $\lambda_3$  were to be very different from  $\lambda_2$ .

## CONCLUSIONS

The relaxation coefficient  $k_r(t)$  for a reversible isomerization, whose long-time limit is  $\lambda_1 = (k_f + k_b)$ , is decomposed into a pair of generalized flux coefficients  $q$  and  $q'$ , and with this separation, it is possible to analyze, in qualitative terms, the differences between the rate constants given by the reversible and irreversible descriptions. With the help of some primitive numerical models, the magnitudes of these differences are explored. When the equilibrium constant for the isomerization is small (we have used the example of  $K_{eq} = 10$ ), in the low-pressure region, the reactive states of both  $R$  and  $P$  are almost in equilibrium, the forward and reverse fluxes are almost equal and, as pointed out by Quack, the magnitude of the reverse flux is a *major* contributor to the smallness of the reaction rate; the true determinant of the reaction rate under these conditions is the rate of deactivation of reactive states of  $P$  to unreactive ones.

On the other hand, when  $K_{eq}$  is large, say  $> 10^3$ , the description of the falloff process begins to approach the traditional description, in which the reduction of the rate of the process  $R \rightarrow P$  at low pressures is caused principally by the depopulation of the reactive states of  $R$ ; the reactive states of  $R$  and  $P$  are now no longer in near-equilibrium, except in the *true* second-order region. Thus, when  $K_{eq}$  is large, our long-

held picture of the falloff process is more-or-less true, which accounts, in part, for its longevity.

That is not to say that all isomerization reactions studied to date have fallen into the large  $K_{eq}$  class: For methyl isocyanide, this is so, since  $K_{eq} \sim 10^{10}$  in the experimental temperature range, but for cyclopropane  $K_{eq}$  is nearer 10, and for most *cis-trans* isomerizations,  $K_{eq}$  will be near unity. Thus, these considerations apply to many famous unimolecular reactions. That they have passed unnoticed until now is due, in large part, to a lack of fundamental interest in the shapes of unimolecular falloff curves (other than in semiempirical methods for fitting them<sup>14</sup>), and to the still very primitive state of our understanding<sup>15</sup> of the interaction between multiexponential relaxation and reactive decay processes in unimolecular reaction systems.

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