

lines at 51% chromium. This supports the view that the chromium dispersion is three-dimensional and very great in this method of preparation. It should be noted that three-dimensional dispersion does not mean that the preparation is necessarily a more effective catalyst.

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Summary

Magnetic susceptibilities have been used, together with X-ray and surface area studies, to elucidate the structure of supported oxides of chromium, molybdenum, tungsten and uranium.

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The Non-Equilibrium Theory of Absolute Rates of Reaction¹

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Introduction

In every formulation of a theory of reaction rates, two distinct problems are involved, the one dealing with the forces acting between the particles participating in the reaction, *i.e.*, the activation energy, and the other, with the calculation of the specific rate constants assuming the first is known. Furthermore, to make the latter calculation possible, a basic assumption is made which finds its origin in S. Arrhenius's^{1b} classical proposal that an equilibrium exists between normal and activated molecules. This is equivalent to the alternate assumption made in the quantum mechanical formulation of rate theory that an equilibrium exists between the various internal degrees of freedom of the initial configuration. The applicability of the equilibrium theory to chemical reactions or to any rate process, in which rearrangement of matter involves surmounting a potential barrier, requires further consideration in view of a complete formulation of the theory of absolute rates of reaction.²

The simplest example of the inapplicability of the simple equilibrium theory is shown for the case of homogeneous gas reactions, where for sufficiently low pressures molecular collisions are inadequate for maintaining an equilibrium concentration in the activated state. For most measurable reactions occurring under normal conditions of temperature and pressure, the assumption appears to be correct. Discussions of this matter are to be found in papers by Marcelin,³ Wynne-Jones and Eyring,⁴ Guggenheim and Weiss⁵ and

others.⁶ The success of the crude collision theory and more so of the theory of absolute rates of reaction, which satisfactorily interprets chemical reactions and many diversified physical phenomena, is strong evidence for the correctness of the equilibrium hypothesis. All this, however, is *a posteriori* evidence that an adequate supply of energetic or activated molecules is maintained during all stages of the reaction and more direct quantitative reasoning is desired. Our present knowledge of chemical dynamics is not sufficiently advanced for a detailed investigation of the individual collision processes which give rise to a very great variety of energetic molecules and to determine what fraction of these fortuitously propitious collisions determine the concentration in the activated state. An ingenious approach to this complex problem was made by H. A. Kramers.⁷ To elucidate the applicability of the absolute rate theory for calculating the velocity of chemical reactions, he considered the effect of the Brownian motion of a medium on the probability of escape of a particle (caught in a potential hole) over a potential barrier. Kramers' results indicate that the theory of absolute rates of reaction gives results correct within 10% over a wide range of viscosity values. Since he employed classical mechanical diffusion theory in the study, it is of interest to take into account the quantized nature of molecular levels.

Method

Consider reactants passing by a series of molecular collisions from a set of energy levels to a subsequent set of levels corresponding to the final states of the products. It is assumed that the values for the specific rate of transition k_{ij} from level *i* to level *j* are known, which, in principle at least, are calculable from the quantum mechanical theory of collisions.⁸ Restricting ourselves to reactions where we can neglect the concentration changes in

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(1a) Allied Chemical and Dye Corporation Research Fellow.

(1b) S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

(2) Also referred to as the "transition-state" method. See M. Polanyi and M. G. Evans, *Trans. Faraday Soc.*, **31**, 875 (1935).

(3) A. Marcelin, *Ann. Phys.*, **3**, 158 (1915).

(4) W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 493 (1935).

(5) E. A. Guggenheim and J. Weiss, *Trans. Faraday Soc.*, **34**, 57 (1938).

(6) Symposium on Kinetics, *ibid.*, 3-81 (1938).

(7) H. A. Kramers, *Physica*, **7**, 284-304 (1940); see also S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943).

(8) N. F. Mott and H. S. W. Massey, "Theory of Atomic Collisions," Oxford University Press, 1933.

all species except A and designating the number in the *i*th level by *A_i*, we have the following set of *n* linear rate equations with constant coefficients

$$\frac{dA_i}{dt} = \sum_{j \neq i} (k_{ji}A_j - k_{ij}A_i) \quad (1)$$

corresponding to the *n* possible energy levels of the reactants and products. Degenerate levels, like other levels, each carry a separate subscript. In each equation of the set (1), the summation extends over all *n* values except *i*. The solution is readily obtained for the set of linear differential equations of the first order with constant coefficients subject to the condition that

$$\sum A_i = D$$

where *D* is the total concentration.

By assuming the solutions *A_i* = *B_i**e^{bt}* where *B_i* is a constant, *b* a parameter and *t* the time, and substituting in the set (1), a simultaneous set of homogeneous algebraic equations is obtained.

$$\sum_{j \neq i} [k_{ji}B_j - (k_{ij} + b)B_i] = 0 \quad (2)$$

These equations are to be satisfied for all values of the *B₁, ..., B_n* which do not all vanish. For this it is necessary and sufficient that the parameter *b* be a root of the auxiliary equation of the *n*th degree, which is obtained from the set (2) by solving the equations for the *B_i*'s by the method of determinants. The auxiliary equation⁹ is

$$\begin{vmatrix} -(\sum_{i \neq 1} k_{i1} + b) & k_{21} & \dots & k_{n1} \\ \dots & \dots & \dots & \dots \\ k_{1n} & k_{2n} & -(\sum_{i \neq n} k_{in} + b) & \dots \end{vmatrix} = 0 \quad (3)$$

By substituting the determined value of the *k*th root *b_k* into equation (2), one is led to the solutions *B_{jk}* = *G_k**C_{jk}*, where for each *j* and *k* one obtains a numerical value for *C_{jk}* and *G_k* is the same arbitrary constant for all *j*'s. Summing all the particular integrals, the general solution of set (1) is

$$A_i = \sum_{k=1}^n B_{ik}e^{b_k t} = \sum_{k=1}^n G_k C_{ik}e^{b_k t} \quad (4)$$

In equation (4), the values of *C_{ik}* and *b_k* are known and by putting *t* = 0 and the *A_i*'s equal to their initial concentrations, the arbitrary constants are readily calculated. Each *A_i* is then a completely determined function of time.

Application to a Specific Model

The following simple case was chosen where the initial state consists of levels 1 and 2 and the final

(9) It is readily shown that one of the *b_k* roots of the secular determinant is zero and the remaining (*n* - 1) roots are all negative as required from physical considerations.

state of levels 3 and 4 with 1 and 4 designated as the levels of lowest energy. This model corresponds to the case of *n* = 4 in the general expressions given above. The rate equations are

$$\begin{aligned} \frac{dA_1}{dt} &= - \sum_{j \neq 1}^4 k_{1j} A_1 + k_{21}A_2 + k_{31}A_3 + k_{41}A_4 \\ \frac{dA_2}{dt} &= k_{12}A_1 - \sum_{j \neq 2}^4 k_{2j}A_2 + k_{32}A_3 + k_{42}A_4 \\ \frac{dA_3}{dt} &= k_{13}A_1 + k_{23}A_2 - \sum_{j \neq 3}^4 k_{3j}A_3 + k_{43}A_4 \\ \frac{dA_4}{dt} &= k_{14}A_1 + k_{24}A_2 + k_{34}A_3 - \sum_{j \neq 4}^4 k_{4j}A_4 \end{aligned} \quad (5)$$

Proceeding according to the general method outlined above, the particular solutions take the form

$$A_i = B_i e^{bt} \quad (i = 1, \dots, 4) \quad (6)$$

To make possible a solution of the characteristic 4th order determinant for the parameter *b* and subsequently, to obtain values for the constants *B₁, ..., B₄*, certain assumptions have to be made with reference to the *n*(*n* - 1) = 12 specific rate constants and proper values chosen to represent their magnitudes.

If we assume that a molecule in the activated state has the same probability for decomposition along the reaction coördinate to any level of the final state, then for the forward process *k₁₃* = *k₁₄* and *k₂₃* = *k₂₄* and similarly for the reverse process, it follows that *k₄₁* = *k₄₂* and *k₃₂* = *k₃₁*. In addition, if we limit ourselves to reacting systems of small heats of reaction, so that the energies of the respective molecular levels in the initial and final states are approximately the same, and combine the resulting relations between the *k_{ij}*'s with those derived on the basis of the first assumption, the following set of relations is found to exist between the twelve specific reaction rate constants of the system

$$\begin{aligned} k_{13} &= k_{14} = k_{41} = k_{42} \\ k_{23} &= k_{24} = k_{24} = k_{31} \\ k_{12} &= k_{43}; k_{21} = k_{34} \end{aligned} \quad (7)$$

To obtain the last two relations where *k₁₂* = *k₄₃* and *k₂₁* = *k₃₄*, it was further assumed that the transmission coefficients of the specific rate constants of a pair of such similar transitions (*i.e.*, activation and deactivation, respectively) are approximately equal. On the basis of the above assumptions for the *k_{ij}*'s, the characteristic 4th order determinant is readily diagonalized to yield the following expressions for the parameter *b* in terms of the four determining rate constants of the initial state *k₁₂*, *k₂₁*, *k₁₃* and *k₂₃*¹⁰

$$\begin{aligned} b_1 &= 0 \\ b_2 &= -(k_{12} + k_{21} + k_{13} + k_{23}) \\ b_3 &= \frac{-\alpha - \sqrt{\alpha^2 - 4\beta}}{2} \\ b_4 &= \frac{-\alpha + \sqrt{\alpha^2 - 4\beta}}{2} \end{aligned} \quad (8)$$

(10) The identity of *k₃₁* is retained to make equation (8) applicable to modification of the 4-level model in the following section.

where

$$\alpha = (k_{12} + k_{21} + 3k_{13} + k_{31} + 2k_{23})$$

$$\beta = [2k_{12}(k_{23} + k_{31}) + 2k_{13}(2k_{21} + k_{31} + 3k_{23})]$$

Choosing the following plausible values for the k_{ij} 's

$$k_{12} = 0.01 \quad k_{23} = 0.1$$

$$k_{21} = 1 \quad k_{13} = 0.001$$

the quantities b_k and in turn C_{ij} have been calculated and are given in Table I. With the particular integrals of equation (6) fully determined, it is only necessary to specify the supplementary conditions for evaluation of the arbitrary constants G_1, \dots, G_4 , which will permit us to obtain the

TABLE I

k	b_k	C_{1k}	C_{2k}	C_{3k}	C_{4k}
1	0	1	0.01	0.01	1
2	-1.306	-1	1.437	-1.437	1
3	-1.111	1	-1	-1	1
4	-6.737	-1	-6.959	6.959	1
	$\times 10^{-3}$		$\times 10^{-3}$	$\times 10^{-3}$	

explicit expressions as to how the population in the four levels varies with time of reaction. We will then be in a position to compare the rates of reaction under equilibrium and non-equilibrium conditions.

Under conditions of equilibrium, the concentrations of the various species A_a defined as n_1, \dots, n_4 are

$$n_1 = \frac{D e^{-\epsilon_1/kT}}{\sum_{j=1}^4 e^{-\epsilon_j/kT}} \quad (9)$$

where D is the total concentration of the molecules A in the system and the statistical weights w for all levels are taken to be equal. From the principle of detailed balance, we have that $k_{ij} = k_{ji} e^{-\epsilon_{ij}/kT}$ where $\epsilon_{ij} = \epsilon_j - \epsilon_i$, so that equation (9) is equally well written

$$n_1 = \frac{D}{\sum_{j=1}^4 \frac{k_{ij}}{k_{ji}}} \quad (10)$$

This represents the supplementary conditions (*i.e.*, when $t = 0$) for the case of equilibrium. For the non-equilibrium case, it is assumed that the concentration of the species A in the lowest level of the initial state (level 1) is at its equilibrium value and the concentrations in all the remaining levels are zero; thus, the supplementary conditions are $A_1 = D/2.02$ and $A_2 = A_3 = A_4 = 0$. The respective arbitrary constants for the two cases have been calculated and are summarized

TABLE II

G_k	Equilibrium	Non-equilibrium
G_1	$D/2.02$	$0.2451 D$
G_2	0	$-1.193 \times 10^{-3} D$
G_3	0	$2.451 \times 10^{-3} D$
G_4	0	$-0.2463 D$

in Table II. The general solution for the case of equilibrium is simply

$$A_1 = \frac{1}{2.02} D$$

$$A_2 = \frac{1}{2.02} \times 10^{-2} D \quad (11)$$

$$A_3 = \frac{1}{2.02} \times 10^{-2} D$$

$$A_4 = \frac{1}{2.02} D$$

where the concentrations in the various levels are constant. Similarly for the case of non-equilibrium, the general solution is

$$A_1 = D[0.2451 e^{b_1 t} + 1.193 \times 10^{-3} e^{b_2 t} + 2.451 \times 10^{-3} e^{b_3 t} + 0.2463 e^{b_4 t}]$$

$$A_2 = D \times 10^{-2} [0.2451 e^{b_1 t} - 0.1714 e^{b_2 t} - 0.2451 e^{b_3 t} + 0.1714 e^{b_4 t}] \quad (12)$$

$$A_3 = D \times 10^{-2} [0.2451 e^{b_1 t} + 0.1714 e^{b_2 t} - 0.2451 e^{b_3 t} - 0.1714 e^{b_4 t}]$$

$$A_4 = D[0.2451 e^{b_1 t} - 1.193 \times 10^{-3} e^{b_2 t} + 2.451 \times 10^{-3} e^{b_3 t} - 0.2463 e^{b_4 t}]$$

where $b_1 = 0$, $b_2 = -1.306$, $b_3 = -1.111$, $b_4 = -6.737 \times 10^{-3}$.

To test the soundness of the equilibrium postulate of the activated complex theory of rate processes, it is required to show to what extent the equilibrium between the initial levels is disturbed, as molecules from the activated state rearrange or decompose into products of the final state. This is best demonstrated by formulating an expression for the ratio of the actual rate to the equilibrium rate for the process and calculating the variation of this ratio Γ with the amount of the substance reacted. Considering the forward rate to be determined by the sum of the velocities from levels 1 and 2 to the final state, the actual velocity is

$$v_a = (k_{13} + k_{14})A_1 + (k_{23} + k_{24})A_2 \quad (13)$$

To calculate the rate of reaction by the theory of absolute rates of reaction, it is assumed that the concentration of the species A_i in the initial state is given by the Maxwell-Boltzmann distribution function. Referring to this velocity as the "equilibrium" rate for the forward process, we have

$$v_o = (k_{13} + k_{14})(A_1 + A_2) \frac{e^{-\epsilon_2/kT}}{\sum_{i=1}^2 e^{-\epsilon_i/kT}} + (k_{23} + k_{24})(A_1 + A_2) \frac{e^{-\epsilon_3/kT}}{\sum_{i=1}^3 e^{-\epsilon_i/kT}} \quad (14)$$

Hence, the ratio Γ of the actual rate to the equilibrium rate is

$$\Gamma = \frac{(k_{13} + k_{14})N_1}{(k_{13} + k_{14}) \frac{e^{-\epsilon_1/kT}}{\sum_{i=1}^2 e^{-\epsilon_i/kT}}} + \frac{(k_{23} + k_{24})N_2}{(k_{23} + k_{24}) \frac{e^{-\epsilon_1/kT}}{\sum_{i=1}^3 e^{-\epsilon_i/kT}}} \quad (15)$$

where $N_1 = A_1/(A_1 + A_2)$ and $N_2 = A_2/(A_1 + A_2)$

are the mole fractions in the initial state. Thermodynamically, the ratio of rate constants is

$$\frac{k_{23} + k_{24}}{k_{13} + k_{14}} = e^{e_{21}/kT} \quad (16)$$

providing that the transmission coefficients of the various rate constants are the same. In addition, from the principle of detailed balance $k_{12} = k_{21}e^{-e_{11}/kT}$ so the expression for the ratio Γ simplifies to

$$\Gamma = \frac{1}{2} \left[N_1 + N_2 \frac{k_{21}}{k_{12}} \right] \left(1 + \frac{k_{13}}{k_{21}} \right) \quad (17)$$

Using the analytical expressions for the mole fractions N_1 and N_2 as determined from the general solution in equation (12) and the chosen values for $k_{12} = 0.01$ and $k_{21} = 1$, the complete expression for the ratio of the actual rate of reaction to the equilibrium rate is given by

$$\Gamma = 0.505 \frac{[0.4902 - 0.1702e^{-1.306t} - 0.2426e^{-1.111t} + 0.4177e^{-6.731 \times 10^{-4}t}]}{[0.2476 - 5.212 \times 10^{-4}e^{-1.306t} + 0.2480e^{-6.737 \times 10^{-4}t}]} \quad (18)$$

To test the validity of the equilibrium postulate of rate theory on the basis of our simple four-level model, we calculate how the velocity ratio deviates from its theoretical equilibrium value of unity with the extent of reaction as determined in this specific case by the concentration of substance A in level 1 of the initial state. Employing equation (18), the variation of the velocity ratio Γ with the concentration A is plotted in Fig. 1. The calculations are summarized in Table III.

TABLE III
VARIATION OF THE RATIO OF ACTUAL TO EQUILIBRIUM RATES WITH AMOUNT OF REACTION

Time, sec.	Γ	A_1 in D units	Amount of ^a reaction % $\frac{[(A_1)_{t=0} - (A_1)_t] \times 100}{(A_1)_0}$
1	0.7967	0.4908	0.87
2	.8858	.4885	1.33
3	.9134	.4865	1.74
4	.9222	.4848	2.08
5	.9251	.4832	2.40
10	.9276	.4754	3.98
100	.9492	.3707	25.1
1000	.9944	.2480	49.9
∞	.9998	.2451	50.5

^a $(A_1)_{t=0} = 0.4951 D$ where D is the total chosen concentration for the system.

The magnitude of the variation of the function Γ is of extreme interest, even though the calculations are based on an extremely simple model. The deviation of approximately 20% in the velocity ratio at the beginning of the reaction represents the over-all error to be expected in the specific rate constant as determined by the theory of absolute rates of reaction. Inasmuch as the calculations were made on an oversimplified model of a reacting system under drastic conditions of non-equilibrium, the results are most gratifying.

In practice, the conditions for rapid restoration of equilibrium concentrations in the activated state will be aided by the multitudinous number of energy levels in any reacting molecular system.

Modifications of the Four-level Model

A more complete analysis of the equilibrium postulate of rate theory according to the general procedure outlined in this paper requires consideration of the following additional points; (1) the effect of the transitions between non-adjacent levels, (2) the magnitudes of the specific rate constants k_{ij} and finally, (3) the comparison of rates of reaction under varied non-equilibrium conditions for the initial state. The same four-level system was considered with the exception that zero values were assigned to all specific rate constants between non-adjacent levels and the magnitudes of the rate constants between the

top levels of the initial and final states (*i.e.*, k_{23} and k_{32}) were increased by a factor of ten. Similar assumptions were made in relating the rate constants between adjacent levels as in the complete solution of the four-level case considered above. The relations between the rate constants together with their chosen values are:

$$\begin{aligned} k_{13} &= k_{21} = k_{14} = k_{41} = k_{24} = k_{42} = 0 \\ k_{21} &= k_{23} = k_{32} = k_{34} = 1 \\ k_{12} &= k_{43} = 0.01 \end{aligned} \quad (19)$$

Two cases of non-equilibrium are considered in relation to this simplified model of the four-level system. In Case I, it is assumed that the con-

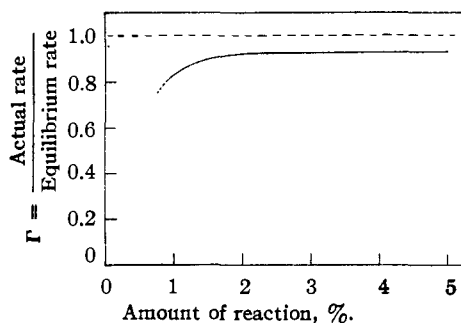


Fig. 1.

centrations in the initial state have their equilibrium values and the concentrations in all the levels of the final state are zero. For Case II, the concentration in the lowest level (level 1) of the normal state is at its equilibrium value and the concentrations in all the other levels of the initial and final state are zero. Case II is similar to the non-equilibrium case investigated in the complete solution of the four-level model. The general solutions (similar to equation (12)) were obtained for the two cases of non-equilibrium and are shown plotted in Figs. 2 and 3 expressed as mole fractions of the respective species of the substance A where the mole fractions are defined as $N_1 = A_1/(A_1 +$

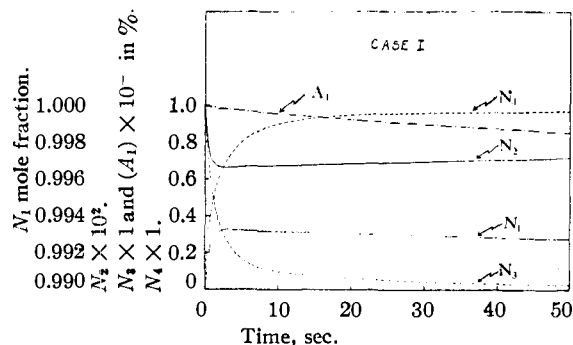


Fig. 2. ---, concentration in level (1); —, normal state; - - - -, final state.

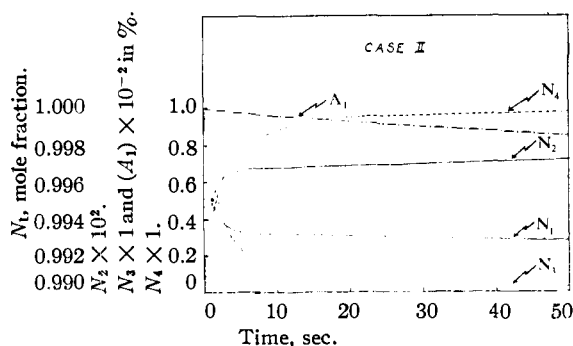


Fig. 3. ---, concentration in level (1); —, normal state; - - - -, final state.

A_2), etc. The general form of these curves in their dependence on time of reaction is characteristic of the general solutions obtained in various modifications of the n -level reacting system. Very rapid variation occurs with time for the various mole fractions and for both Case I and II, equilibrium values are obtained in approximately 1000 seconds. These are given in Tables IV and V for the two respective cases of non-equilibrium.

TABLE IV

Case I, Initial Conditions: $A_1 = D/1.01$; $A_2 = D/1.01 \times 10^{-2}$; $A_3 = A_4 = 0$

t , sec.	N_1	$N_2 \times 10^2$	$N_3 \times 10^2$	N_4
0	0.9901	0.9901	*	*
1	.9931	.6798	59	0.42
10	.9932	.6732	9.91	.902
100	.9923	.7676	1.679	.9834
1000	.9901	.9893	0.9909	.9901
∞	.9901	.9901	.9901	.9901

* Indeterminate.

TABLE V

Case II, Initial Conditions: $A_1 = D/1.01$; $A_2 = A_3 = A_4 = 0$

t , sec.	N_1	$N_2 \times 10^2$	$N_3 \times 10^2$	N_4
0	1.0000	0	*	*
1	0.9951	0.4742	73	0.32
10	.9932	.6722	10.9	.891
100	.9922	.7667	1.687	.9831
1000	.9901	.9779	1.002	.9899
∞	.9900	.9900	0.9900	.9900

* Indeterminate.

Of particular interest is the variation with the time of reaction of the mole fractions in level 2, since, in the absence of the transitions between non-adjacent levels, it determines the rate of the forward reaction. This is compared with the amount of reaction which is primarily determined by the concentration in level 1. The variation of the concentration A_1 expressed as a per cent. is also included in Figs. 2 and 3. In Case I, the mole fraction for level 2 drops to a minimum value of 67% of its equilibrium value in two seconds and the equilibrium value is attained in one thousand seconds. This represents the order of variation of 33% to be expected in the over-all specific rate constant for this modified version of the four-level system.

A second modification of the original model was considered to study the effect of varying the magnitudes of the rate constants. It is similar to the model treated above with the one exception that the transition constants for the top levels of the initial and the final states (*i.e.*, k_{23} and k_{32}) were reduced by a factor of ten. Here, a general solution was obtained for the non-equilibrium case, where the concentrations in the initial state have their equilibrium values and the concentrations in the levels of the final state are zero (which is similar to Case I of non-equilibrium used for our first modified model above). For this simplified treatment of the four-level system a maximum error of 8.2% in the over-all specific rate constant was found during the course of the reaction. A summary of the calculations based on modifications of the original four-level system of twelve rate constants is presented in Table VI.

In columns 3 and 4, the maximum variation of the velocity ratio function Γ is compared with the amount of reaction. This represents the error to be expected in the over-all reaction rate constant as calculated by the equilibrium theory of absolute rates of reaction. The small variation in the function Γ of 8.2% from its equilibrium value of unity for the modified model (2) indicates that the values chosen for the rate constants between non-adjacent levels of our original model are slightly large. Comparison of the respective times for the attainment of a maximum variation in the function Γ in this case indicates the important role played by the rate constants between non-adjacent levels in rapid restoration of equilibrium. By increasing the magnitude of the rate constants between the top levels of the initial and final states for the modified model (1), more rapid restoration of equilibrium concentrations is attained at the expense of a larger error in the ratio Γ . A comparison of the results for the two cases of non-equilibrium for the simplified model (1) indicates that for more drastic conditions of non-equilibrium as given by Case II, the error in the over-all specific rate constant is increased by 2% together with a slightly longer time for restoration of the high equilibrium rate of reaction.

TABLE VI

Model	Non-equilibrium cases	$\Gamma = \frac{\text{Actual rate}}{\text{equilibrium rate}}$	Amount of reaction, %	Time, sec.
$k_{13} = k_{14} = k_{41} = k_{42} = 0.001$ $k_{23} = k_{32} = k_{24} = k_{31} = 0.1$ $k_{12} = k_{43} = 0.01$ $k_{21} = k_{34} = 1$	Case II: $A_1 = D/2.02$ $A_2 = A_3 = A_4 = 0$	0.80	0.87	1
1) $k_{13} = k_{31} = k_{24} = k_{42} = k_{14} = k_{41} = 0$ $k_{23} = k_{32} = k_{21} = k_{34} = 1$ $k_{12} = k_{43} = 0.01$	Case I: $A_1 = D/1.01$ $A_2 = (D/1.01) \times 10^{-2}$ $A_3 = A_4 = 0$ Case II: $A_1 = D/1.01$ $A_2 = A_3 = A_4 = 0$.67 .65	.87 .90	2 3
2) $k_{13} = k_{31} = k_{24} = k_{42} = k_{14} = k_{41} = 0$ $k_{23} = k_{32} = 0.1$ $k_{21} = k_{34} = 1$ $k_{12} = k_{43} = 0.01$	Case I: $A_1 = D/1.01$ $A_2 = (D/1.01) \times 10^{-2}$ $A_3 = A_4 = 0$.918	.87	10

Our modified model (1) of the four-level system especially for the Case II of non-equilibrium is in every respect analogous to the problem of simultaneous chemical reactions. The end species A_1 and A_4 are the stable reactant and product, respectively, whereas A_2 and A_3 are the unstable concentrations. This case is an addition to similar ones treated by A. Skrabal¹¹ in his series of papers on the subject of simultaneous chemical reactions. This treatment applies directly to unimolecular reactions with or without an inert gas and to bimolecular or higher order reactions where one reactant is in much lower concentration than the others. Other cases which lead to non-linear equations provide special mathematical difficulties, but the results would be similar.

(11) A. Skrabal, *Monatsh.*, **24**, 293 (1943), and earlier papers.

Summary

The results obtained taking into consideration the quantized nature of molecular energy levels in testing the applicability of the equilibrium theory of absolute rates of reaction are essentially in agreement with the results found by H. A. Kramers. The general procedure employed complements the classical diffusion approach to this problem. Further application of this treatment to more complicated systems ($n > 4$) is deemed necessary in order to indicate what refinements are to be made in the theories of reaction rates. The first author wishes to acknowledge his appreciation of the privileges extended to him by the University of Utah where the greater part of this research was carried out.

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Ultraviolet Absorption Spectra of Substituted Vinyl Aromatic Monomers and Polymers¹

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In applying the ultraviolet absorption method of Meehan³ to the analysis of copolymers of butadiene with various substituted styrenes and other aromatic vinyl type monomers, it was necessary to obtain the absorption spectra of the polymers of each of the monomers for calibration purposes. Since the absorption maxima most useful for analytical purposes lie in the wave length range 250–300 μ , the data were restricted to this region.

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(3) E. J. Meehan, *J. Polymer Sci.*, **1**, 175 (1946).

Absorption data were also collected for some of the monomers in the same wave length range, inasmuch as it was necessary to prove the complete removal of monomers from the polymers and copolymers. A small amount of residual monomer would lead to a large error because of its relatively intense absorption.

Experimental

The freshly distilled monomers, synthesized by the Organic Division,⁴ were polymerized in bulk by irradiation with ultraviolet light. A 1 to 2 ml. sample of monomer in

(4) C. S. Marvel, *et al.*, *THIS JOURNAL*, **67**, 2250 (1945); **68**, 786, 861, 1085, 1088 (1946); R. L. Frank, *et al.*, *ibid.*, **68**, 1365, 1368 (1946).