

## The Absolute Rates of Heterogeneous Reactions I. The General Theory of Adsorption

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The article by Thorne Lay and Hiroo Kanamori is an excellent review of the energy released by the 1994 Chilean earthquake. The authors estimate that the earthquake released approximately five times as much energy as a 100-megaton atmospheric nuclear explosion. This is a significant finding, as it suggests that the energy released by earthquakes can be comparable to that of nuclear weapons. The authors also discuss the potential for using seismic energy release as a variable that depends on the nuclear deformation of a nuclear device. I believe the authors underestimate the total strain energy release by a factor of about 3, or 10 times, depending on the fault plane. Accounting for total strain energy release would increase the earthquake energy number by orders of magnitude.

Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

This article does not have any references.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon, later becomes released in a new event. Perhaps calculations of one added that in, while another's calculations did not. E.M.C.  
Written by Edgar McCarroll, 14 July 2012 19:59

excited level the lifetime is derived from the *total* probability of transition, that is, the sum of the  $a_{ki}$  values.

The computation of the lifetime, which is nearly the same for all initial levels of the same band, was carried through for the initial level of  $Q_1(4\frac{1}{2})$ . From the same level the fainter lines  $R_1(3\frac{1}{2})$  and  $Q_{R_{12}}(4\frac{1}{2})$  originate (neglecting two very faint satellites). From the intensity formulae of the Hill-Van Vleck theory the relative intensities of these lines follow, respectively, as 2.10; 0.63; 0.24. The next change of *vibrational* quantum number which belongs to the  $0 \rightarrow 1$  emission band is very improbable, as indicated by the relatively very small intensity of the 3428 band; hence all transitions from  $v' = 0$  to higher vibrations of the lower electronic level can be disregarded. In this respect the computation of the lifetime is much simpler for OH than for many other molecules. Furthermore, we assumed that there is no other *electronic* transition competing with the 3064 band since no other band system of the neutral hydroxyl is known.

The resulting lifetime is  $3.8 \times 10^{-6}$  sec. On the other hand the lifetime to be expected at the wave-length 3100A, computed from the radiation damping of the corresponding electromagnetic

dipole, is  $0.4 \times 10^{-8}$  sec. The smaller value of the actual lifetime indicates a half-forbidden transition.

This long lifetime has a bearing on certain results on the persistence of rotation in collisions. In preceding papers abnormal rotation of OH as produced by the discharge and its persistence in collisions was discussed.<sup>25</sup> A few cm of He added hardly affected the observed abnormal rotation. In all the estimates a normal lifetime of the order of magnitude  $10^{-8}$  sec. was assumed. On the basis of our present results the lifetime is much longer and therefore the chance for collisions during the lifetime much higher. Lyman and Jenkins,<sup>26</sup> in careful photometric work, found that the addition of 2 cm He to a discharge through H<sub>2</sub>O caused only a minor reduction of the high rotation. With our value of the lifetime (applying the gas kinetic cross section of the water molecule to the excited OH radical), we computed that 570 collisions during the lifetime are rather inefficient in bringing about thermal equilibrium.

<sup>25</sup> O. Oldenberg, Phys. Rev. **46**, 210 (1934).

<sup>26</sup> E. R. Lyman and F. A. Jenkins, Phys. Rev. **53**, 214 (1938).

## The Absolute Rates of Heterogeneous Reactions

### I. The General Theory of Adsorption\*

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The statistical theory of reaction rates, developed by Eyring for homogeneous reactions, is extended to include heterogeneous reactions. It is shown that rates of adsorption and desorption are governed by the same form of mathematical expression in terms of partition functions of the system as rates of homogeneous reactions, provided only that for the activated state a "super-partition function," formed by adding together the partition functions for all the active spots, is used. The pseudothermodynamical form of the rate constant form is discussed, and illustrated by applications to special cases.

IT has been shown by Eyring<sup>1</sup> that the rate constant  $k_1$  of a homogeneous chemical reac-

tion may be represented by an expression of the form

$$k_1 = \kappa \frac{kT}{h} \frac{Z^*}{\prod_i Z_i} \quad (1)$$

\* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

<sup>1</sup> Eyring, J. Chem. Phys. **3**, 107 (1935); Eyring and Wynne-Jones, J. Chem. Phys. **3**, 492 (1935).

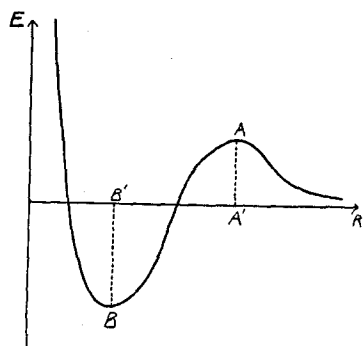


FIG. 1.

where  $k$  is Boltzmann's constant,  $T$  the absolute temperature,  $h$  is Planck's constant, and  $\kappa$  is the transmission coefficient, i.e. the fraction of the molecules reaching the critical configuration which react.  $\Pi_i Z_i$  is the product of the partition functions of the reactants and  $Z^*$  is the partition function for the "pseudo-molecule" formed at the critical configuration.

We wish here to discuss the modifications which are necessary to extend the theory to include adsorption processes. The chief differences between the heterogeneous and the homogeneous cases are (1) the adsorbent surface will in general be composed of a large number of "active spots" at which adsorption may take place, and (2) adsorption will generally be limited to a unimolecular layer. The total number of active spots is not, however, usually equal to the total number of molecules which can be adsorbed by the surface. Instead, each active spot is a gateway, through which each molecule being adsorbed must pass, leading to a more or less extensive hinterland. Until this hinterland is completely filled, the active spot will remain active. We may, however, treat as special cases surfaces in which the active spots may hold either a single molecule or an infinite number.

A typical potential energy curve for a molecule in the adsorption process is shown in Fig. 1. In most cases there will be some activation energy to be overcome. This is represented by the hump with its top at  $A$ . The activation energy itself is given by  $AA'$ . The molecule finally reaches a point of equilibrium at  $B$ . The heat of adsorption is given by  $BB'$ . The point  $B$  is not necessarily the final position of the molecule:

there may be other points on the surface with greater binding energies, separated from  $B$  by other activation passes. If these passes are higher than  $A$ , the rate of adsorption will be determined by the rate of passage over the secondary humps. For the present, however, we shall assume that the rate of adsorption is determined by the rate of passage over the hump  $A$ .

Neither the activation energy nor the heat of adsorption will be constant as we go from active spot to active spot. In fact it may be the case that these quantities depend not only on the active spot itself, but also on whether or not the neighboring spots are occupied. For the sake of simplicity, however, we shall assume that each spot is characterized by a definite activation energy and energy of adsorption. The active spots may then be divided into types, each type with its characteristic potential surface. In particular each type will have its own activation energy and heat of adsorption. We shall denote the number of active spots of the  $\alpha$ th type which are not completely filled by  $K^{(\alpha)}$ . At the beginning of adsorption each  $K^{(\alpha)}$  will be simply equal to the total number of active spots of the  $\alpha$ th type,  $K_0^{(\alpha)}$ , but as adsorption goes on  $K^{(\alpha)}$  will gradually decrease.

In order to make the definitions of "adsorbed" and "desorbed" molecule exact, we shall imagine the potential surface for each spot to be divided by two parallel planes at a small distance  $\delta$  apart, at the summit of the activation hill, and perpendicular to the direction of motion of a molecule following the path of least resistance. Any molecule which is in the region between the inner plane and the surface we shall call an adsorbed molecule; any molecule between the planes, an activated molecule; and any molecule outside the planes, a desorbed molecule.

The molecules of the system can then be divided into groups: (1) the molecules adsorbed on an active spot of the  $\alpha$ th type, (2) molecules activated at an active spot of the  $\alpha$ th type, (3) desorbed molecules. For each of these groups of molecules there can be set up a partition function. We shall denote the partition functions for these three groups by  $Z_a^{(\alpha)}$ ,  $Z_0^{(\alpha)}$ , and  $Z_d$ . We shall also let  $N_a^{(\alpha)}$ ,  $N_0^{(\alpha)}$ , and  $N_d$  be the numbers of molecules in the three groups.

By an obvious generalization of a well-known theorem of statistical mechanics<sup>2</sup> the values of  $N_a^{(\alpha)}$ ,  $N_0^{(\alpha)}$ , and  $N_d$  when the whole system is at equilibrium are given by

$$N_d : N_a^{(\alpha)} : N_0^{(\alpha)} = Z_d : K^{(\alpha)} Z_a^{(\alpha)} : K^{(\alpha)} Z_0^{(\alpha)}. \quad (2)$$

This gives immediately

$$N_0^{(\alpha)} = N_d K^{(\alpha)} Z_0^{(\alpha)} / Z_d \quad (3)$$

for the number of activated molecules.

Following Eyring<sup>1</sup> we shall assume that during the actual adsorption process the desorbed molecules remain essentially in statistical equilibrium. We also assume that the activated molecules moving toward the surface are also in equilibrium with the desorbed molecules. Eyring's argument then gives immediately for the rate of adsorption on the spots of the  $\alpha$ th type

$$\kappa \frac{kT}{h} N_d \frac{K^{(\alpha)} Z_*^{(\alpha)}}{Z_d}, \quad (4)$$

where we have now put

$$Z_0^{(\alpha)} = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} \delta Z_*^{(\alpha)}, \quad (5)$$

$Z_*^{(\alpha)}$  being the partition function for a molecule "frozen" in place at the top of the potential barrier.

The total rate of adsorption on the whole surface is then

$$\kappa \frac{kT}{h} \frac{N_d}{Z_d} \sum_{\alpha} K^{(\alpha)} Z_*^{(\alpha)}. \quad (6)$$

Remembering that any partition function is of the form  $\sum_i e^{-E_i/kT}$ , where the sum is over all possible energy levels, and  $E_i$  is the energy of the  $i$ th level, we see that the expression  $\sum_{\alpha} K^{(\alpha)} Z_*^{(\alpha)}$  in (6) is of the same nature as a single partition function. It consists of a sum of terms of the form  $e^{-E_i/kT}$ , but in it every energy level for every active spot is included, even exact duplicates being counted as many times as they appear. If we denote this "super-partition

function"  $\sum_{\alpha} K^{(\alpha)} Z_*^{(\alpha)}$  by  $Z^*$ , (6) becomes

$$\kappa \frac{kT}{h} \frac{N_d}{Z_d} Z^* \quad (7)$$

and the rate constant for the adsorption,  $k_a$ , becomes

$$k_a = \kappa \frac{kT}{h} \frac{Z^*}{Z_d}. \quad (8)$$

Formally, this equation is exactly the same as (1), but it must be remembered that in (1)  $Z^*$  represents the partition function for a *single* type of activated molecule, while in (8)  $Z^*$  is the *sum* of the partition functions for the activated points of all the active spots.

It is interesting to note that (7) reduces to the "classical" expression for the number of collisions with a surface if the appropriate assumptions are made. These are (1) that the surface is a plane surface of area  $S$ , (2) that the molecules may be treated as mass points, and (3) every collision is effective, i.e., there is no activation energy of adsorption and  $\kappa=1$ . If we introduce these assumptions into our theory we find

$$Z_d = \frac{(2\pi mkT)^{\frac{1}{2}}}{h^3} V,$$

while  $Z^*$  reduces to the partition function for a two-dimensional gas

$$Z^* = \frac{2\pi mkTS}{h^2}.$$

Hence the rate of collision is, by (7)

$$\left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}} \frac{N_d S}{V}, \quad (9)$$

which is identical with the classical expression.

Instead of using the partition functions, it is sometimes convenient to use instead the more usual thermodynamic functions of the system. For systems at equilibrium the relation between these is

$$Z = N e^{-F/RT}, \quad (10)$$

where  $Z$  is the partition function for the system,  $N$  is the number of molecules in the system, and

<sup>2</sup> Cf. Fowler, *Statistical Mechanics*, second edition (Cambridge, 1937), p. 160.

$F$  is the chemical potential (partial molal free energy). It must be born in mind that the dependence of the right side of (10) on  $N$  is only apparent, for  $Z$  is independent of the number of molecules. Because of this fact, it is not necessary to use the value of  $F$  for the actual state of the system, and it is equally valid to use the value of  $F$  in any arbitrarily chosen standard state at the same temperature, provided that the number of molecules,  $N$ , be taken to be the number in the standard state. Neglect of this fact has led to needless controversy in the past.

We may formally use (10) for the partition function  $Z^*$  as well as  $Z_d$ . The corresponding chemical potential  $F^*$  will then not be a true thermodynamic quantity, but behaves mathematically in exactly the same way as a chemical potential.

In terms of  $F_d$ , the chemical potential of the desorbed molecules, and  $F^*$ , Eq. (8) becomes

$$k_a = \kappa \frac{kT}{h} \frac{N^*}{N_d} e^{-(F^* - F_d)/RT}. \quad (11)$$

If we choose an arbitrary standard state for the desorbed and activated states, and moreover choose them in such a way that  $N^* = N_d$ , then

$$k_a = \kappa (kT/h) e^{-\Delta F^*/RT}, \quad (12)$$

where  $\Delta F^* = F^* - F_d$ . Separation of  $\Delta F^*$  into an entropy and heat content of activation by

$$\Delta F^* = \Delta H^* - T\Delta S^*$$

then gives

$$k_a = \kappa (kT/h) e^{\Delta S^*/R} e^{-\Delta H^*/RT}. \quad (13)$$

Before this theory can be applied, it is necessary to obtain some idea as to the values to be expected for  $\Delta S^*$  and  $\Delta H^*$ . For gases, the standard state usually chosen is that in which the pressure is one atmosphere. The number of molecules in the standard state is then  $N_d = P_0 V/kT$ , where  $P_0 = 1.013 \times 10^6$  dynes/cm<sup>2</sup>. In order to use Eqs. (12) and (13) it is therefore necessary to choose as the standard state for the activated molecule one in which the same number,  $P_0 V/kT$  of molecules are in the activated state: i.e. the pseudothermodynamic functions for the activated state will depend on the volume of the gas phase! This results in rather "queer" values

of the entropy of the activated molecules, as will be seen presently.

For the purposes of rough estimates, the motion of a molecule may be considered in terms of translations, rotations, and vibrations. Each degree of translational freedom is characterized by a mass,  $m$ ; each rotation by a moment of inertia,  $I$ , if two dimensional, or three moments,  $A$ ,  $B$ , and  $C$ , if three dimensional; each vibration by a frequency,  $\nu$ , or a characteristic temperature  $\Theta = h\nu/k$ . The contributions of each of these motions, the "zero-point energy" (which includes the energy of activation), and the terms arising from the choice of standard state through the factor  $N$  in (10) to  $H$  and  $S$  are well known and are shown in Table I. The typical values given are for a temperature of 300°K, a mass of one atomic weight unit, a moment of inertia of  $10^{-40}$  g cm<sup>2</sup> and a characteristic temperature  $\Theta$  of 500°K.

An examination of the numerical values of  $H$  and  $S$  shows the following important facts: the zero-point energy contributes nothing to  $S$ , but appears *in toto* in  $H$ . The remaining terms in  $H$  are of the order of a few times  $RT$ . The value of  $H$  is therefore chiefly determined by the value of  $E_0$ , provided  $E_0$  is not too small. On the other hand, the entropy is very sensitive to quantum effects. Thus we see that vibrations will even at fairly high temperatures contribute little to the entropy. The rotations contribute an appreciable amount, but much less than the translations.

The "standard state" correction will always cancel out when the difference between two entropies is taken, unless the total number of particles changes, when it becomes an important part of the entropy change. Because of the large negative value of this term for the usual standard state for gases, the entropies calculated for the adsorbed molecules come out with large negative values. This seeming contradiction to the concept of positive entropies is, however, only apparent, for the "standard state" we are forced to use is one which would be impossible to realize. (The entropy of a perfect gas could theoretically be made negative by a sufficient increase of pressure, because of the term  $-R \ln P$ . The necessary value of  $P$  is, however, about  $10^5$  atmospheres.)

Considering now the adsorbed (or activated)

molecules, there are two cases of great importance as simplified models. The first is that in which we may consider the adsorbed molecules as a two-dimensional gas. Omitting the terms due to the internal motions of the molecules, the entropy of such a two-dimensional gas is seen from Table I to have the form

$$S = R \ln \frac{2\pi m (kTe)^2 A}{h^2 P_0 V}, \quad (14)$$

where  $A$  is the area of the surface. The corresponding form for the three-dimensional desorbed gas is

$$S = R \ln \frac{(2\pi m)^{3/2} (kTe)^{5/2}}{h^3 P_0}. \quad (15)$$

The entropy of either adsorption or activation in this case is then

$$\Delta S^* = R \ln \frac{hA}{(2\pi mkTe)^{1/2} V}, \quad (16)$$

which is, then, the entropy of activation for the "classical" collision picture. It should be noticed, however, that for any molecules except those consisting of a single atom, there will also be an "internal" entropy of activation. In particular the rotation of the free molecules will be reduced to either two-dimensional rotations, or to vibrations. This will lead to a marked decrease

in entropy for such molecules, i.e. to a greatly reduced rate of adsorption.

The other case is that in which the adsorbed molecules are firmly bound to the surface, so that the motion is purely vibrational. As a very highly idealized example, let us consider a model in which the molecules are adsorbed in such a fashion that the energy quantum of each vibration is so high that practically all the adsorbed molecules are in their lowest states, and that even at the top of the potential barrier the only possible motion is one translational degree of freedom. We shall refer to this as the case of "tight" adsorption. In this case the partition function  $Z^*$  is simply  $K_0$ , the total number of active spots which are empty. The entropy of the activated molecules is then

$$S^* = R \ln \frac{K_0 e k T}{P_0 V}. \quad (17)$$

Now an upper limit to  $K_0$  is  $10^{16}$  spots per square centimeter. At  $300^\circ\text{K}$ ,  $S^*$  (referred to the usual standard state) is less than  $-13$  cal./degree. Comparing this with the "classical" value of  $S^*$ , which is  $-12.7$  cal./degree, we see that there is no sharp boundary between the two cases. In fact, the case of "tight" adsorption can be treated essentially as a "classical" adsorption if an area of about  $10^{-16}$  cm<sup>2</sup> is assigned to each active spot.

TABLE I. Table of contributions to the partial molal heat content and partial molal entropy. The translational contribution is per unit length. The vibrational contribution is the limiting form for low temperatures. The typical values are for the constants given in the text.

TYPE OF MOTION	CONTRIBUTION TO		TYPICAL VALUES	
	$H$	$S$	$H$	$S$
Zero-point energy	$E_0$	0		0
Translation (1 dimension)	$1/2 RT$	$R \ln \frac{(2\pi mkTe)^{1/2}}{h}$	300	37.6
Rotation (2 dimensions)	$RT$	$R \ln \frac{8\pi^2 I k T e}{h^2}$	600	6.0
(3 dimensions)	$3/2 RT$	$R \ln \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kTe)^{3/2}}{h^3}$	900	10.1
Vibration	$R\Theta e^{-\Theta/T}$	$R(1 + \Theta/T)e^{-\Theta/T}$	190	0.4
Standard State	$RT$	$R \ln \frac{kTe}{PV}$	600	-87.9

There is, however, one important difference between these cases. This arises from the saturation effects which may be expected from the case of "tight" adsorption. If each active spot can hold only one molecule, then we must expect to find the value of  $K_0$  decreasing as adsorption goes on. Beside this direct effect on the reaction rate, another secondary effect may enter if the active spots show a wide range of values for their free energies of activation, for then the first adsorption will take place on those spots which show the smallest free energies of activation. The reaction velocity in these cases will show a very marked decrease with time.

As an example, let us consider the data of Burwell and Taylor<sup>3</sup> on the adsorption of  $H_2$  on chromic oxide gel. Burwell and Taylor measured the rates of adsorption of  $H_2$  (maintained at constant pressure) on this catalyst over the temperature range 195°K–491°K. The mechanism of the adsorption is evidently complex, for there is at each temperature a very rapid initial adsorption, followed by a slower adsorption. It was found, however, that if the initial adsorption is subtracted from the data at each temperature, the resulting time-adsorption curves are all similar. In fact if a "reduced" time  $t'$ , defined by

$$t' = te^{-21,700/RT} \quad (18)$$

is substituted for the actual time,  $t$ , the "corrected" adsorption curves are identical. Burwell and Taylor did not attempt to analyse this curve further. I have made an exponential analysis of these data, and have found that all of them can be represented very closely by the equation

$$y = y_0 + 1.8(1 - e^{-k_1 t'}) + 13.8(1 - e^{-k_2 t'}) + 39.0(1 - e^{-k_3 t'}), \quad (19)$$

in which  $y$  is the total amount adsorbed (cc of  $H_2$  at  $STP$ ) and  $y_0$  is the initial adsorption, the rate of which is too fast to measure. The constants  $k_1$ ,  $k_2$ , and  $k_3$  have the values  $1.08 \times 10^{10}$ ,  $6.36 \times 10^8$ , and  $9.88 \times 10^7$  min.<sup>-1</sup>, respectively.

The form of Eq. (19) makes it clear that even the slow adsorption is not a simple process. An equation of this type can be obtained from a

number of mechanisms, of which the simplest to assume would be one in which adsorption was taking place simultaneously at four different varieties of active spots. It is well known that if the rate of adsorption at one of the kinds of active spot were  $k'$  and the rate of desorption  $k''$ , the total amount adsorbed in time  $t$  would be

$$k'/k''(1 - e^{-k''t}).$$

We can therefore regard (19) as the sum of four such expressions, the first having a very large value of  $k''$ . It is thus a simple matter to find the other three pairs of values of  $k'$  and  $k''$ . Expressing these in terms of the corresponding heats and entropies of activation, we obtain the result shown in Table II. The value 21,700 for the  $\Delta H^*$  of all the processes involved is an immediate consequence of the fact that the time enters Eq. (19) only through  $t'$ .

Another, and equally good mechanism is one in which adsorption is followed by a series of consecutive, reversible reactions on the surface, e.g. a process in which the adsorbed molecules move away from the active spots to other unoccupied parts of the surface. While it is impossible to give any simple relation between the rate constants for these reactions the final form of the integrated rate expression is again of the same form as Eq. (19). It must be noted, however, that in this case too the values of  $\Delta H^*$  for all the reactions involved must again be 21,700 cal., for the same argument which led to this result in the previous case still applies.

While other mechanisms are possible, these two seem the most plausible, and we shall confine our discussion to these. Considering the first of these mechanisms in the light of the present theory, two facts stand out at once. The first is that the value of  $\Delta H^*$  is the same for all processes. This would be an extraordinary coincidence if the four adsorption processes were all independent, as this mechanism assumes. Moreover it implies a vanishing heat of adsorption, which is contrary to experience. Secondly, the values of  $\Delta S^*$  in Table II are not those we have been led to expect for adsorption processes, but much larger. We are therefore forced to regard the first mechanism as highly improbable.

The second mechanism meets with less difficulty. In this case the true adsorption rate is the

<sup>3</sup> Burwell and Taylor, J. Am. Chem. Soc. **58**, 697 (1936).

TABLE II.

	ADSORPTION		DESORPTION	
	$\Delta H^*$	$\Delta S^*$	$\Delta H^*$	$\Delta S^*$
$k_1$	21,700	-20	21,700	-21
$k_2$	21,700	-22	21,700	-27
$k_3$	21,700	-24	21,700	-31

rate of the initial adsorption. It is unfortunate that the data do not permit an evaluation of this rate. The other rates involved are the rates of migration of the molecules (or possibly atoms) of hydrogen over the surface. It is still somewhat remarkable that the heats of activation are equal for all the processes involved, but such a situation is by no means inconceivable. That the heat of the reactions should vanish is not surprising, for the migration might very well lead to a new position of the same energy as that of a molecule adsorbed on an active spot.

The most plausible explanation of the data would then seem to be a process taking place in a series of steps. The first step is the adsorption proper on the active spots of the catalyst. The energy of activation of this process is probably much lower than the 21,700 characteristic of the later steps. This is followed by a process of migration, or "hopping" over the surface away from the active spots. There would seem to be at least three varieties of potential passes through which this process can take place, all with nearly the same height (21,700 cal.) but differing from each other in shape, so that the entropies of

TABLE III.

$t^\circ\text{C}$	$k$ CC/MIN.	$k_{\text{cor}}$ CC/CM <sup>2</sup> SEC.	$\Delta F^*$	$\Delta S^*$	$\Delta H^*$
0	3.72	$2.70 \times 10^{-3}$	19,200	-55.0	4,100
15	5.87	4.25	20,000	-55.8	3,900
25	7.62	5.52	20,500	-56.3	3,800
35	9.55	6.92	21,100	-56.9	3,600
45	11.81	8.56	21,700	-57.4	3,400
55	14.26	10.33	22,300	-58.0	3,200
65	16.93	12.27	22,800	-58.5	3,100

activation at the different passes are different, thus leading to different absolute rates for the various reactions.

As a second example, this time of adsorption from solution, let us consider the data of Van Name<sup>4</sup> on the reaction between cadmium metal surfaces and  $I_2$  (or  $I_3^-$ ). The rate constants given by Van Name are reproduced in Table III, together with the free energies, heats, and entropies of activation calculated from them. The rate constants are given first in Van Name's units, and then in the column  $k_{\text{cor}}$  when reduced to unit area and to sec.<sup>-1</sup>. It will be noticed that in this case the entropies of activation are in good agreement with the values we should expect from the results of this paper. From the values of  $\Delta H^*$  it is impossible to say whether or not the rate governing step is or is not diffusion to the surface. This is certainly just about the value we should expect for such a process, and the entropy of a diffusion process would not be appreciably different from that of an adsorption.

<sup>4</sup> Van Name, Am. J. Sci. **43**, 453 (1917).