

THE RATES OF ATOMIC REACTIONS

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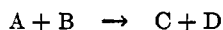
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Received December 3, 1931

The number of investigations concerning free atoms and radicals is rapidly growing. A large amount of information dealing with their various properties is now available. The extent of this experimental and theoretical information necessitates considerable limitations to be imposed on the scope of the present review and only quantitative data concerning homogeneous gaseous reactions of free atoms will be discussed.

THE EXCHANGE REACTIONS

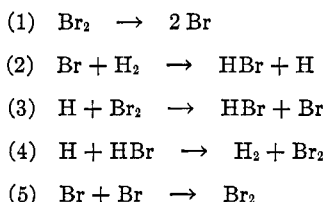
In 1919 Herzfeld (1), Christiansen (2) and Polanyi (3) propounded the theorem that gaseous exchange reactions of the type



where A is an atom with free valences, require no activation energy if the process is exothermic and require therefore an activation energy equal to the heat of reaction if the process is endothermic. Thus the rate of such exothermic reactions can be represented by the rate of gas kinetic collisions, multiplied eventually by a "steric factor" which takes care of the necessity of definite orientation in the moment of collisions. It was assumed to be not far from unity. The rate of endothermic reactions, accordingly, is represented by a similar expression multiplied by the heat of reaction in an exponential function. For a considerable time all experimental observations seemed to support this theory. The absence of activation energy was established in a number of atomic reactions. Simultaneously some information on the magnitude of the steric factor became available.

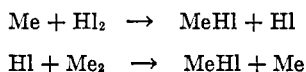
The original justification for the theory was obtained from an

analysis of the experimental data of Bodenstein and Lind (4) on the thermal hydrogen-bromine reaction. These data, enriched in the meantime by the study of the photochemical reaction (5), show conclusively that the reaction proceeds through the steps:



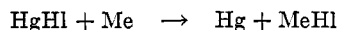
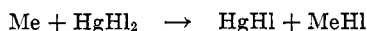
Of these, reaction 2 is endothermic to the extent of 17,000 cal. and reactions 3 and 4 are exothermic. The conclusion that the latter two do not require an activation energy was arrived at from the knowledge that their velocity ratio (equal to eight, owing to a steric factor) is constant over a very wide temperature range. Thus an identical activation energy must be associated with both these processes and the value zero appears most likely. The temperature coefficient of the photochemical process points to reaction 2 as having an activation energy equal to the (negative) heat of reaction, unless reaction 5 has also an activation energy. Furthermore, if such an activation energy is assumed for reaction 2, the rate of reaction 5 is calculated in agreement with the triple collision theory, as will be seen later.

Numerous examples of atomic exchange reactions without activation energy have been discovered by Polanyi and his coworkers (6) in their studies of the "highly dilute flames"—reactions of alkalis and some other metallic vapors with gaseous halogens and some halides at very low pressures. The reactions of alkalis (Me) and halogens (HI) occur according to the scheme:



Both the steps are exothermic and, according to Polanyi, occur with a velocity which shows that the reactions do not require an activation energy. Similar results were obtained in the study of

the reactions of alkalis with volatile halides of divalent metals, which also occur in two exothermic steps:



Neither of these requires an activation energy. Shay (7) studied recently the reaction of alkalis with hydrogen halides. He found that the rate of reaction of sodium with hydrogen chloride, which is endothermic to the extent of some 5000 cal., is about .01 of the number of kinetic collisions at 600°K and is about .04 at 700°K. These figures, substituted in the equation

$$\frac{\text{Reaction rate}}{\text{Collision number}} = e^{-\epsilon/KT}$$

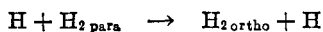
give as the activation energy 5500 and 4600 cal., in good agreement with the value for the heat of reaction. The use of the above equation implies, of course, that the steric factor is equal to unity. The activation energy, however, cannot be less than the heat of reaction in endothermic processes and the above result shows that in the sodium-hydrogen chloride reaction the steric factor is very near unity. The reactions of sodium with hydrogen bromide and hydrogen iodide and those of potassium with hydrogen chloride and hydrogen bromide are accompanied by no appreciable heat changes. They occur on every collision as nearly as can be established. The reaction of potassium and hydrogen iodide, finally, which is exothermic to the extent of some 5000 cal., occurs about ten times faster than would be anticipated from the number of kinetic collisions. The same is true of the first step in the reactions of sodium with halogens mentioned above. All these processes occur already when the reactants approach each other to a distance of 10Å.

The semiquantitative work of Boehm and Bonhoeffer (8) on hydrogen atoms indicates that their reactions, not only with bromine, but also with other halogens and with hydrogen sulfide, occur at room temperature with a rate not far below the rate of kinetic collisions. No accurate estimates of the steric factor can be made for these reactions.

Some time ago London (9) pointed out that, from the quantum mechanical point of view, reactions of free atoms should require activation energy, but in amounts normally less than those characteristic of reactions of molecules with saturated valences. Since then a large number of atomic reactions with activation energy has been studied and the already discussed cases, where no activation energy was found, appear as exceptions rather than as a rule. One of the atomic reactions requiring activation energy was known prior to the publication of London. It is the reaction of chlorine atoms with hydrogen molecules. Coehn and Jung (10) have established that in very dry hydrogen-chlorine mixtures no measurable reaction occurs on illumination, although it is known that chlorine atoms are produced. To account for the lack of reaction, the reaction rate of chlorine atoms with hydrogen molecules must be so slow that an activation energy well in excess of 10,000 cal. appears necessary. Also, if hydrogen atoms are involved in the chain, their reaction with hydrogen chloride must require an activation energy of several thousand calories, since the latter substance does not inhibit the main reaction. A more direct evidence of atomic reactions with activation energy was obtained by Kistiakowsky (11), who found that the reaction rate of excited oxygen atoms in the 1D state with hydrogen molecules was less than 10^{-4} of the number of collisions, thus necessitating an activation energy of at least 5000 cal. The rate of this reaction with non-excited atoms, according to Kistiakowsky, is probably still slower. According to Harteck and Kopsch (12) the reaction which non-excited oxygen atoms undergo with hydrogen molecules is, undoubtedly, $O + H_2 \rightarrow OH + H$. From the collision yield (10^{-8}) at room temperature they estimate the activation energy to be 8000 cal., from the temperature coefficient $E = 6000 \pm 1000$ cal. It is possible, therefore, that the steric factor of this reaction is considerably below unity. The same authors find that the reaction of oxygen atoms with methane requires about 7000 cal. as calculated from the collision yield at room temperature, and that the reaction $H_2O + O \rightarrow O_2 + H_2 + 1500$ cal. is still much slower. Kistiakowsky and Millington (13) find that the reaction between excited oxygen atoms and methane is as

slow as the reaction with normal atoms. Thus it seems to be established that the presence of electronic excitation energy in the atom does not preclude the necessity of additional activation energy of kinetic and vibrational origin. This is in accord with the views of London.

Farkas (14) and more recently Geib and Harteck (15) have thoroughly investigated the reaction



finding that it requires 7200 cal. and that the steric factor is about 0.1.

Schumacher (16), from considerations of the mechanism of the photochemical ozone decomposition, concludes that the reaction $\text{O} + \text{O}_3 = 2 \text{O}_2$ occurs in one out of 2000 collisions at room temperature, which corresponds to 4500 cal. activation energy if the steric factor is unity.

v. Hartel and Polanyi (17) have succeeded in finding, by the method of "highly dilute flames," a large number of reactions requiring activation energy. All of these involve sodium and organic halides and proceed according to the scheme

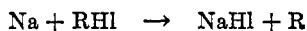


Table 1 summarizes their results and shows quite obvious regularities in such a series as the methyl, ethyl, phenyl monohalides or in the series of mono-, di-, tri- and tetra-chloromethanes.

These figures have been computed by the comparison of the reaction velocities, measured around 250°C., with the collision numbers, and involve the assumption that the steric factors are equal to unity. While this assumption is not far from the correct one in some instances, it may lead to quite wrong results in other cases. Thus v. Hartel and Polanyi find, from the temperature coefficient of the sodium-methyl chloride reaction, an activation energy of 7500 cal. in satisfactory agreement with the otherwise calculated value. On the other hand, the negligible temperature coefficient of the sodium-cyanogen reaction points to an activation energy of not more than 2000 cal., while from the reaction rate v. Hartel and Polanyi calculate 12,000 cal. Here the steric

TABLE 1
Activation energies in reactions of sodium with organic halides

COMPOUND.....	CH ₃ I	CH ₃ Br	CH ₃ Cl	CH ₃ F	C ₂ H ₅ I	C ₂ H ₅ Br
ACTIVATION ENERGY.....	0	3200	8800	>25000	1700	4400
COMPOUND.....	C ₂ H ₅ Cl	C ₆ H ₅ I	C ₆ H ₅ Br	C ₆ H ₅ Cl	CH ₂ Cl ₂	CHCl ₃
ACTIVATION ENERGY.....	7300	0	3100	7200	4900	2000
COMPOUND.....	CCl ₄	CH ₂ CHCl ₂	CH ₂ CHCl ₂	1-C ₃ H ₇ I	1- <i>i</i> -C ₅ H ₁₁ Cl	
ACTIVATION ENERGY.....	0	5800	4900	3000	5400	
COMPOUND.....	C ₆ H ₅ CH ₂ Cl	CH ₃ COBr	CH ₃ COCl	C ₆ H ₅ COCl	CICN	
ACTIVATION ENERGY.....	0	2100	1700	0	2000	

factor is of the order of 10^{-4} . The authors attribute this to a shielding by nitrogen atoms of the carbon-carbon bond which is disrupted in the reaction with sodium.

Summing up the discussed data on the exchange reactions, it is found that the activation energies range from zero to more than 25,000 cal., but ordinarily are of the order of several thousand calories. The steric factor varies at least by a factor of 100 in reactions involving diatomic molecules and is capable of still larger variations in atomic reactions with polyatomic molecules.

THE ADDITION REACTIONS

The other atomic reactions which received considerable attention are association reactions,



which have been thoroughly discussed theoretically. Experimental material however is still quite meagre, although there is no lack of attempts to study such reactions. This type of atomic reaction was brought into the focus of general interest by a paper of Born and Franck (18), in which the authors concluded that the direct addition reaction is highly improbable in the case of atoms. Their reasoning is that the energy of the complex formed on the collision of two atoms and equal to the heat of reaction plus the kinetic energy of the relative motion of the particles is usually different from the amounts which the molecule can take up as the quantized energy of the electronic excitation and nuclear vibration. Accordingly, the complex is unstable and must fall apart within a time comparable to the time of one half oscillation of the molecule, unless a third body—a gaseous molecule, an atom or a solid surface—colliding with the complex takes away a part of the energy and thus stabilizes the molecule. From these assumptions the equation can be readily derived:

$$\frac{d(C)}{dt} = \frac{k_1 k_2 (A)(B)(N)}{\frac{1}{\tau} + K_2(N)}$$

where (A) , (B) and (C) are the concentrations of the reactants and of the product, (N) is the concentration of molecules acting as the

“third body,” K_1 and K_2 are the velocity constants of the complex forming and of the stabilizing processes, and τ is the mean life of the complex. If τ is of the order of 10^{-13} seconds, while $K_2(N)$ is of the order of collision frequency, i.e., 10^{10} at atmospheric pressure, the above equation is simplified to:

$$\frac{d(C)}{dt} = K_1 K_2 \tau (A)(B)(N)$$

If K_1 is also of the order of collision frequency, the rate, as given by this equation, is of the same order of magnitude as the rate of triple collisions. The latter are defined as those collisions in which a third molecule is within molecular distance from the center of two colliding molecules.

The equation has received an experimental confirmation in the work of Jung and Jost (19) who determined the rate of the recombination of bromine atoms from a study of the hydrogen-bromine reaction. They found that at atmospheric pressure and 500°K about 0.005 of all collisions between bromine atoms lead to molecule formation and that the yield is proportional to the total gas pressure, hydrogen and bromine being present. Assuming that K_1 and K_2 are kinetic collision frequencies, τ is calculated from Jung and Jost's data to be 3×10^{-13} sec., while the inverse of the fundamental frequency of the bromine molecule is $\frac{1}{\nu_0} = 2 \times 10^{-13}$ sec. This excellent agreement should be taken however with some reservations, because Jung and Jost find that argon and helium are less than 0.1 as efficient as hydrogen and bromine in stabilizing the complex. This shows that K_2 is not necessarily equal to the kinetic collision frequency and that the stabilization is a selective process. The equalling of K_1 to collision frequency can be sometimes doubted also, because Jackson and Kistiakowsky (20) find that the reaction $\text{O} + \text{CO} + \text{N} = \text{CO}_2 + \text{N}$ proceeds some 100 times slower than the reaction $\text{O} + \text{O}_2 + \text{N} = \text{O}_3 + \text{N}$. The introduction of a “steric factor” into the equation seems to be appropriate here.

Although a very large amount of work has been devoted to the study of the recombination of hydrogen atoms, the results are still

not completely certain. Smallwood (21), Senftleben and Rieche-meier (22), and Steiner and Wicke (23) agree that the rate at low pressures is given approximately by the number of triple collisions, although they disagree on the magnitude of the "steric factor." On the other hand, it is claimed (24) that in the Langmuir atomic arc hydrogen atoms can be blown out to the distance of several centimeters at atmospheric pressure. This indicates that the recombination rate is slower than the rate of triple collisions by several orders of magnitude and suggests that the other results may be ascribed to heterogeneous reactions.

Since the appearance of Born and Franck's paper two other mechanisms of atomic recombination have been discussed. Polanyi and Wigner (25) consider a process which is essentially the reversal of the optical Auger process (predissociation) or of the mechanism of unimolecular decomposition as developed by Rice and Ramsperger (26). If the energy of the colliding atoms (or radicals), including the heat of molecule formation and their relative kinetic energy, happens to be equal to one of the quantized energy levels of the molecule,¹ a radiationless transition may occur in the moment of collision whereby the energy is redistributed and a relatively stable molecule results. The probability of this process is not infinitely small because the quantized levels have a finite breadth. The semistable molecule will then either reverse the process of energy distribution and fall apart again, or it will emit the energy as radiation or lose it on collisions. The kinetic treatment of these assumptions leads to the equation:

$$\frac{d(C)}{dt} = K_1(A)(B) \frac{K_2(N) + \frac{1}{\tau'}}{\frac{1}{\tau} + \frac{1}{\tau'} + K_2(N)}$$

where (A) , (B) , (C) and (N) have the same meaning as before, K_1 is the rate constant of the association process, K_2 the constant of the

¹An excited electronic level in diatomic molecules, and either that or a state in which the energy is distributed among vibrational degrees of freedom in polyatomic molecules.

stabilization process by collision, and τ and τ' are the mean lives of the semistable molecule with respect to the decomposition and the emission of radiation. The former is probably of the order of 10^{-10} or 10^{-11} seconds (27), the latter of the order of 10^{-8} seconds. If $K_2(N)$ is equal to collision frequency, the equation reduces at moderate pressures to:

$$\frac{d(C)}{dt} = \frac{K_1 K_2(A)(B)(N)}{\frac{1}{\tau} + K_2(N)}$$

It is then formally identical with the triple collision equation. The velocity constants have, however, a quite different meaning. K_1 is now considerably smaller than the collision frequency, because, for the success of association, the energy of colliding particles must lie within prescribed limits. A further restricting condition is imposed by the Franck-Condon principle. τ , on the other hand, is considerably larger, so that the reaction becomes trimolecular only at lower pressures. In the case of atoms this type of association reaction is probably negligibly slow as compared with the triple collision mechanism on account of widely spaced energy levels of diatomic molecules, but the associations of radicals and large molecules may be predominantly of this type (28). However this reaction must take place in the case of atoms also. Thus, an S_2 molecule is known to possess a predissociation spectrum (29) and a recombination of the atoms under emission of radiation is here required by the principle of entire equilibrium.

The third recombination process, discussed by Frenkel and Semenov (30) is a reversal of Franck's (31) "dissociation in one elementary act." It involves the collision of an excited and a normal atom, radiation being emitted in the instant of collision, so that an electronically nonexcited molecule is produced in one of its vibrational quantum states. The necessary requirement for the occurrence of this process is, according to the Franck-Condon principle, that the atoms approach to a distance which is within the intranuclear distance range of the normal vibrating molecule. Kondratjew and Leipunsky (32) think that the luminescence emitted by the flames of burning hydrogen halides is due to

such a recombination of halogen atoms. Urey and Bates (33) studied the process more in detail and confirm the suggestion of Kondratjew and Leipunsky. The velocity constant of this reaction can be calculated by considering the equilibrium between the black body radiation and a dissociating gas, provided the light absorption coefficients in the region of the continuous spectrum are known for all vibrational states of the normal molecule. Urey and Bates estimate, from other considerations, the probability of such a process on collision of an excited and a normal atom to be about 10^{-5} .

The processes which were discussed on the preceding pages cover the field of homogeneous atomic reactions, although admittedly only a part of the available material has been utilized here. A large amount of interesting information is available now on the heterogeneous reactions of free atoms. This was assumed to be outside the scope of the present review.

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