40. The value of the remaining terms in k_∞ will not be qualitatively affected by the representation of $V(r)$ by a 12–6 Lennard-Jones potential, for which it is found that $U(r^+) = 0.8E_0$ and $r^+ = 1.23r_e$. The final result is

$$k_\infty \approx \nu e^{-\beta E_0} (r^+/r_e)^2[2\beta U(r^+)]^{1/3}\,\Gamma(2/3) \approx 2.1\,(\beta E_0)^{1/3}\,\nu e^{-\beta E_0} \quad (14)$$

The explicit use of the centrifugal potential thus tends to increase k_∞ over its familiar value $\nu e^{-\beta E_0}$ (see ref. 1, for example), which is obtained by taking the critical coördinate at infinity. This result may be of interest in view of the high values of the pre-exponential factors of some unimolecular rate constants at the high-pressure limit.

Appendix

It is the purpose of this appendix to illustrate that at finite pressures Slater's criterion of "interesting" states is inconsistent with the random phase assumption.[11] Here it is sufficient to consider the second order limiting rate constant k_0 for the simple case of a non-rotating harmonic oscillator. This system is characterized by the Hamiltonian

$$H = p^2/2\mu + \mu\omega^2q^2/2 \qquad (A1)$$

with interesting states defined by $q < q_0$ and $H \geqslant E_0 = \mu\omega^2 q_0^2/2$. The trajectory time s^* for these states is readily found to be

$$s^* = \frac{1}{\nu}\left(1 - \frac{\cos^{-1}\sqrt{E_0/H}}{\pi}\right) \qquad (A2)$$

where ν is the natural frequency of the oscillator. The limiting rate constant may be exhibited in the alternative forms

$$k_0 = \nu\beta \int_{E_0}^{\infty} e^{-\beta H}\, s^*(H)\mathrm{d}H \qquad (A3)$$

or

$$k_0 = \nu\beta \int_{J_0}^{\infty} \int_{q\,<\,q_0} e^{-\beta H}\,\mathrm{d}J\mathrm{d}\psi \qquad (A4)$$

Equation A4 is written in terms of the angle variable ψ and action variable $J = H/\nu$. The inequality $q < q_0$, defining the interesting states, restricts the angle variable to

$$0 \leqslant \psi \leqslant 1 - \frac{\cos^{-1}\sqrt{J_0/J}}{\pi} \qquad (A5)$$

so that upon substitution and partial integration

$$k_0 = e^{-\beta E_0} - \frac{e^{-\beta E_0}}{\pi}\int_0^{\infty}\frac{e^{-\beta E_0 u^2}}{1 + u^2}\,\mathrm{d}u \qquad (A6)$$

The first term of eq. A6 constitutes the random phase assessment of k_0. The correction term possesses an upper bound given by

$$-\,k_0 + e^{-\beta E_0} = e^{-\beta E_0}/2\sqrt{\beta E_0 \pi} \qquad (A7)$$

For representative cases of $\beta E_0 \approx 40$, the correction term decreases k_0 about 5%.

This example illustrates that the time scales for the collisional activation process and the subsequent dissociation require future clarification. Thus, vertical activation processes which would exclude states with $q < -q_0$ would double the correction in eq. A7.

[11] See N. B. Slater, *Proc. Roy. Soc.* (*London*), **A194**, 112 (1948), p. 119, for comment on this point.

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY, UNIVERSITY OF OXFORD, OXFORD, ENG.]

The Recombination of Halogen Atoms

BY MARGARET I. CHRISTIE

RECEIVED JUNE 27, 1962

Previous results on iodine atom recombination in the presence of rare gases have shown that the measured rate of recombination in a mixture containing a very low ratio of molecular iodine to rare gas is less than that calculated from the additive effect of molecular iodine and rare gas as third bodies. It is suggested that, under these conditions, the deactivation of the vibrationally excited iodine, formed as the initial product of the recombination, is the rate-determining step. The data for iodine and bromine atom recombination are discussed in relation to the various mechanisms of atomic recombination which have been proposed.

The recombination of atoms in the gas phase

$$\mathrm{X + X + M = X_2 + M'}$$

follows the kinetic law

$$\mathrm{d(X_2)}/\mathrm{d}t = k_B\mathrm{(X)^2} = k_M\mathrm{M(X)^2}$$

In a mixture of gases

$$k_\mathrm{B} = \sum_M k_\mathrm{M}\,\mathrm{M}$$

where k_M is the third-order constant relating to species M. The function of the third body, M, is to remove some of the excess energy possessed by the two atoms and thus allow formation of the diatomic molecule.

The first extensive work on iodine and bromine atom recombination was that of Rabinowitch[1] who derived values of k_M for a variety of gases from photostationary measurements. The development of flash photolysis has made possible the direct measurement of the recombination of iodine[2–7] and bromine[4,8] atoms. Iodine values for k_M for some thirty gases have now been obtained; the values vary over a range of a thousand, helium

[1] E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 283 (1937).

[2] K. E. Russell and J. Simons, *Proc. Roy. Soc.* (*London*), **A217**, 271 (1953).

[3] M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *ibid.*, **A231**, 446 (1955).

[4] R. L. Strong, J. C. W. Chien, P. E. Graf and J. E. Willard, *J. Chem. Phys.*, **26**, 1287 (1957).

[5] D. L. Bunker and N. Davidson, *J. Am. Chem. Soc.*, **80**, 5085, 5091 (1958).

[6] R. Engleman and N. R. Davidson, *ibid.*, **82**, 4770 (1960).

[7] G. Porter and J. A. Smith, *Proc. Roy. Soc.* (*London*), **A261**, 28 (1961).

[8] W. G. Givens and J. E. Willard, *J. Am. Chem. Soc.*, **81**, 4773 (1959).

being the least effective and molecular iodine the most effective third body so far discovered. In general the agreement in absolute values obtained by different investigators is good, but there is disagreement[3,5] as to the value of k_{I_2} (8.5×10^{17} cc.^{2} mole^{-2} sec.$^{-1}$ or 1.9×10^{18} cc.^{2} mole^{-2} sec.$^{-1}$ at room temperature). The difference lies not in the experimental results but in their interpretation. The value for molecular iodine is derived from measurements of recombination in a mixture of molecular iodine and an inert gas. Christie, Harrison, Porter and Norrish[3] found marked deviations from the relationship $k_B = k_{I_2}I_2 + k_M M$ when the ratio of I_2/M was low. If these deviations are real then the lower value of k_{I_2} is probably the more accurate. A possible explanation for these results at low ratios of I_2/M is suggested in this paper.

Possible mechanisms of halogen atom recombination are discussed.

Recombination of Iodine Atoms at Low Ratios of I_2/M.—The results obtained[3] for the recombination of iodine atoms in presence of the five rare gases, over a range of I_2/M ratios, are plotted in Fig. 1. The results for the highest I_2/M ratios have been omitted as their accuracy is uncertain because of thermal effects which produced apparent deviations from second-order kinetics in this range. Since $k_B = k_{I_2}I_2 + k_M M$ the plot of k_B/M against I_2/M should be linear, the gradient giving the value of k_{I_2}, and the intercept the value of k_M. From the data for argon, which are the most extensive, a value of 8.7×10^{17} cc.^{2} mole^{-2} sec.$^{-1}$ for k_{I_2} is obtained. At very low ratios of I_2/M, however, the recombination is slower than predicted from the above relationship and values of k_B/M even less than k_{Ar} are observed. For the other rare gases similar results were obtained, the gradient being independent of the rare gas. For helium measurements were not made below the ratio of $I_2/He = 2.5 \times 10^{-4}$ and no deviation was observed. For the other gases k_B/M at low I_2/M ratios was always lower than expected, the deviations being most marked for xenon. The values of k_M obtained are given in Table I. They differ slightly from those of reference 3 because of the omission of the less reliable data. The values of $(I_2/M)_{dev}$ are the approximate values of I_2/M below which recombination is less rapid than expected. Within the accuracy with which $(I_2/M)_{dev}$ can be ascertained, the ratio is proportional to k_M. In the same region of I_2/M, Strong, Chien, Graf and Willard[4] similarly found low values of recombination constants and the results of Bunker and Davidson[5] at 29° could also be interpreted in this way, although the authors themselves have not done so.

TABLE I

RATE CONSTANTS FOR THE INERT GASES

Gas	He	Ne	Ar	Kr	Xe
10^{-15} k_M, cc.^{2} mole^{-2} sec.$^{-1}$	1.21	1.72	3.26	4.08	5.55
10^4 $(I_2/M)_{dev}$	..	3	4	5	7
Relative k_M (mechanism B)	1.82	1.97	(3.26)	4.02	5.51

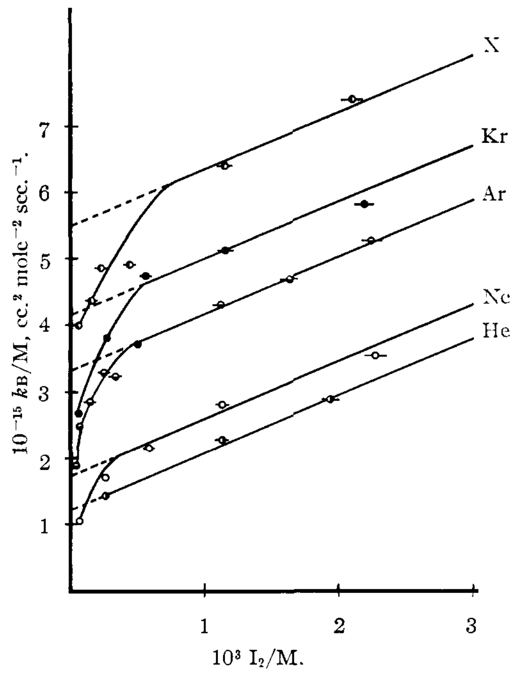

Fig. 1.—The variation of k_B/M with I_2/M for the five rare gases: ◑, He; ○, Ne; , ⊖Ar; ○, Kr; ◐, Xe.

Experimentally the recombination was followed by the reappearance of molecular iodine as measured by its absorption in a wave length region extending from 4900 to 5600 Å. From the vibration frequency and the potential energy curves for iodine[9] it can be estimated that molecules in the vibrational levels 1 and 2, as well as those in the ground vibrational level, would contribute to absorption in this region. Although it is almost certain that the iodine molecules are initially formed in vibrational levels just below the dissociation level,[10,11] it has always been assumed that the recombination process 1 is the rate-determining step; *i.e.*, that

$$I + I + M \longrightarrow I_2^{\ddagger} + M' \qquad (1)$$

$$I_2^{\ddagger} + M \longrightarrow I_2 + M' \qquad (2)$$

process 2 is relatively rapid. If different gases have the same relative efficiency in the two processes then the assumption is justified. If, however, molecular iodine is very much ($>10^4$) more efficient than the rare gas in deactivating vibrationally excited iodine so that 2 is essentially $I_2^{\ddagger} + I_2 \rightarrow 2I_{2v<3}$ even at very low ratios of I_2/M where the contribution of iodine to the over-all recombination 1 is negligible, then reaction 2 would become the rate-determining step if $k_2(I_2^{\ddagger})(I_2) < k_M(I)^2M$. Then $(I_2/M)_{dev} = k_M(I)^2/k_2\ (I_2^{\ddagger})$ and for similar experimental conditions $(I_2/M)_{dev}$ should be proportional to k_M as found experimentally. Under the conditions used the mean concentration of iodine atoms is $\sim 10^{-10}$ mole/cc. and, estimating the concentration of I_2^* to be $\sim 10^{-11}$ mole/cc., k_2 for $M = I_2$, $\dot{\sim}$ 10^{10} cc. mole^{-1} sec.$^{-1}$.

Information about the transfer of vibrational energy from iodine in the excited electronic state

---

(9) L. Mathieson and A. L. G. Rees, *J. Chem. Phys.*, **25**, 753 (1956).

(10) J. C. Polanyi, *ibid.*, **31**, 1338 (1559).

(11) J. K. Cashion and J. C. Polanyi, *Proc. Roy. Soc.* (*London*), **A258**, 529 (1960).

$^3\pi_{0_u}v' = 26$ is available from fluorescence studies.[12] The results show that only one or two vibrational quanta are transferrred at a time and, assuming a life-time of 10^{-6} sec. for the excited iodine molecule,[13] that the collision efficiency of the rare gases is about one in ten. The transfer of vibrational energy into kinetic energy becomes increasingly difficult as the quanta increase in size so that several thousand collisions with molecular iodine are required to transfer vibrational energy from the first vibrational level of the ground state.[14] However, vibrational exchange processes of the type $I_{2\ v=0} + I_{2\ v=2} \rightarrow 2I_{2\ v=1}$ would suffice to bring the iodine down to low lying vibrational levels ($v < 3$) and could explain the particular efficiency of iodine. The value derived for k_2 for iodine is not unreasonable. It may be compared with the rate constant of 10^8 cc. mole^{-1} sec.$^{-1}$ recently found[15] for the deactivation by nitrogen of vibrationally excited nitrogen to levels below the fourth. Vibrationally excited iodine has not been detected spectroscopically in experiments on the flash photolysis of iodine. In view of the much lower sensitivity of photographic methods of detection compared with photoelectric, this is not surprising because only low concentrations of vibrationally excited iodine would be present even under favorable conditions. A possible test of the suggested mechanism could be made by using different frequencies of monitoring light to follow the recombination. Vibrationally excited hydrogen chloride, formed by the recombination of hydrogen and chlorine atoms, has been detected by its absorption in the infrared region.[11]

The Mechanism of Recombination.—The third-order recombination may be considered to take place as a result of triple collisions.[1] The first collision may be between two iodine atoms.

Mechanism A

$$\mathrm{I} + \mathrm{I} \rightleftarrows \mathrm{I_2}^* \qquad (3)$$

$$\mathrm{I_2}^* + \mathrm{M} \longrightarrow \mathrm{I_2}^{\ddagger} + \mathrm{M} \qquad (4)$$

or, between an iodine atom and a molecule M.

Mechanism B

$$\mathrm{I} + \mathrm{M} \rightleftarrows \mathrm{IM}^* \qquad (5)$$

$$\mathrm{IM}^* + \mathrm{I} \longrightarrow \mathrm{I_2}^{\ddagger} + \mathrm{M} \qquad (6)$$

where I_2^* and IM^* have energy in excess of that required for dissociation and $I_2^{\ddagger}$ is vibrationally excited iodine.

The "complex" theory[5,7,16] of atomic recombination is a modification of mechanism B; since, under normal experimental conditions, M >> I, IM^* will undergo many collisions with M before reaction 6 can take place and an equilibrium concentration of "bound" IM, *i.e.*, IM with energy less than that required for dissociation, may be formed.

Mechanism C

$$\mathrm{I} + \mathrm{M} \rightleftarrows \mathrm{IM}^* \qquad (5)$$

$$\mathrm{IM}^* + \mathrm{M} \rightleftarrows \mathrm{IM} + \mathrm{M} \qquad (7)$$

$$\mathrm{IM} + \mathrm{I}^{\ddagger} \longrightarrow \mathrm{I_2} + \mathrm{M} \qquad (8)$$

The iodine formed in reaction 8 is also likely to be vibrationally excited as the reaction is of the type[17] in which much of the energy of the reaction appears as vibrational energy in the newly formed bond. Reaction 2, the deactivation of $I_2^{\ddagger}$, is not rate determining under ordinary experimental conditions.

The results for the rare gases should be the simplest to interpret theoretically. Rate constants calculated for mechanism A, assuming a collision time of 10^{-13} sec. for I_2^*, are of the correct order of magnitude, but the relative order of efficiencies predicted for the rare gases is the reverse of that found experimentally.[18] In order to calculate rate constants for mechanism B, an estimate of T_{IM}, the time during which I and M can be considered to be in collision is required. If a method based on the Sutherland viscosity constants, as suggested by Rabinowitch,[1] is used, the relative values predicted for the rare gases are in good agreement with experiment (Table I). The experimental rate constant for argon corresponds to the reasonable collision time of 2.5×10^{-13} sec. It is difficult to judge the success of any particular theory[1,5,7,19,20] in predicting absolute values of the rate constants because of the uncertainty over the appropriate statistical factor to be used. Theoretically only $^1/_{16}$ of the collisions between two $^2P_{3/2}$ iodine atoms can result directly in the formation of a ground state iodine molecule, but there are other weakly attractive states. From the absolute magnitude of the rate constants for the rare gases it is difficult to avoid the conclusion that practically every collision between iodine atoms in the presence of a third body results in the formation of a stable molecule. If this is so the larger rate constants for other gases must be attributed to increasing interaction between I and M, resulting either in an increased collision time (mechanism B) or in an equilibrium concentration of IM (mechanism C) and not to increasing efficiency of energy transfer.

The results for all gases are plotted in Fig. 2, the values for the rare gases and for iodine being those derived from Fig. 1 and the values for other gases from references 2, 6 and 7. There is a fairly good correlation between log k_M and T_C, the critical temperature of gas M, showing that the factors which determine T_C, *i.e.*, the intermolecular forces characteristic of M, are largely responsible[2] for determining k_M. Least squares treatment gives the relationship log $k_M = 15.19 + 3.26 \times 10^{-3}\ T_C$, which reproduces the experimental values of k_M within a factor of about two for most gases, including the rare gases for which a complex mechanism is least likely and molecular iodine for which the complex mechanism has been considered most likely.

Information about bromine atom recombination is much less extensive than for iodine. The greater

---

(12) C. Arnot and C. A. McDowell, *Can. J. Chem.*, **36**, 114 (1958).

(13) B. Stevens, *ibid.*, **37**, 831 (1959).

(14) R. J. Dwyer, *J. Chem. Phys.*, **7**, 40 (1939).

(15) J.E. Morgan, L. F. Phillips and H. I. Schiff, *Disc., Faraday Soc.*, in press (1962).

(16) G. Porter, *Disc. Faraday Soc.*, in press (1962).

(17) N. Basco and R. G. W. Norrish, *ibid.*, in press (1962).

(18) M. I. Christie, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc. (London)*, **A216**, 152 (1953).

(19) E. P. Wigner, *J. Chem. Phys.*, **5**, 720 (1937); **7**, 646 (1939).

(20) J. C. Keck, *ibid.*, **29**, 410 (1958); **32**, 1035 (1960).

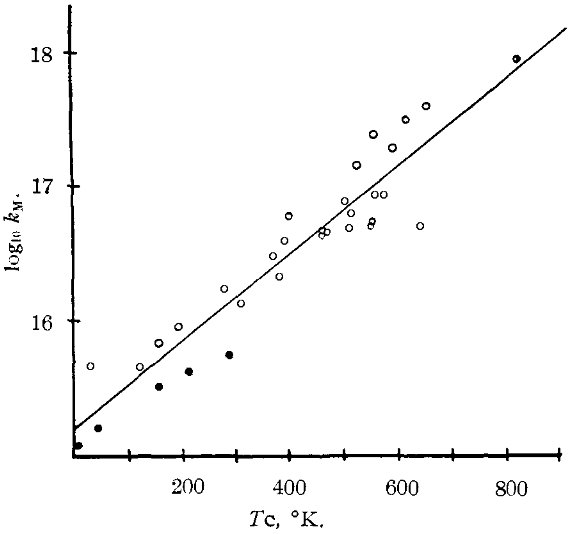

Fig. 2.—The variation of k_M for iodine atom recombination with the critical temperature of M: ●, rare gas; ◑, iodine; ○, other gases; ——, $\log_{10} k_M = 15.19 + 3.26 \times 10^{-3} T_C$.

reactivity of bromine molecules, combined with a smaller absorption coefficient, make accurate determinations more difficult; the reactivity of bromine atoms restricts the range of substances which can be studied. The values obtained by the photostationary method[1] are in reasonable agreement with those obtained by the method of flash photolysis.[4,8] The most efficient third body is molecular bromine, but there is some doubt[8,21,22] as to the exact value of k_{Br_2}. The values obtained in these investigations are plotted in Fig. 3. Within the experimental uncertainty log k_M for bromine atom recombination shows the same dependence on T_C as does log k_M for iodine recombination and for the same third body, the values of the recombination constants for iodine and bromine atoms are very similar.

It has been shown that mechanism B is adequate to explain the rate constants for the rare gases. Bunker and Davidson[5] have carried out statistical calculations for a number of other gases. Although the relative efficiencies of the gases can probably be explained equally well by either mechanism B or by mechanism C, mechanism C is to be preferred because it has the added advantage of explaining the negative temperature coefficients of k_M in terms of the dissociation energy of "bound" complex IM. Values of $-E_M$, assuming that the rate constant k_M can be expressed as $k_M = A_M e^{-E_M/RT}$, range from ~0.5 kcal. for helium to 4.4 kcal. for iodine.[18] (If the value derived in this paper for k_{I_2} at room temperature is correct, however, $-E_{I_2}$ may be less than 3 kcal.) These values correspond to bond energies higher than predicted for van der Waals forces and Porter and Smith[7] have suggested that the complexes are charge transfer ones. This would be consistent with the fact that the values of log k_M for the rare gases fall below the average line while those for the aromatic hydrocarbons and the alkyl iodides, which have rather lower ionization potentials than would be expected from their critical temperatures, tend to fall above the average line (Fig. 1).

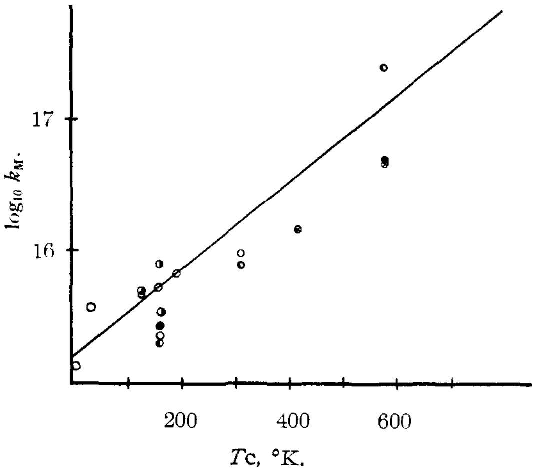

Fig. 3.—The variation of k_M for bromine atom recombination with the critical temperature of M: ○, ref. 1; ◑, ref. 4; ◐, ref. 8; ●, ref. 21; ⊗, ref. 22; ——, $\log_{10} k_M = 15.19 + 3.26 \times 10^{-3} T_C$.

Other explanations of the negative temperature coefficients are possible. Polanyi[10] has calculated that dissociation from the higher vibrational levels in which the iodine is initially formed could account for an apparent negative activation energy of at least 0.85 kcal. This would be increased if greater weight were given to the possibility of two or three quanta transfers in this region of small vibrational quanta. It is possible that such an effect could explain the increasing of the negative temperature coefficient with k_M.

Palmer and Hornig[23] introduced the energy transfer theory, which takes account of degrees of freedom other than translational in the energy transfer steps, in order to account for the high pre-exponential factors and the form of the temperature dependence for the reverse dissociation reactions. There is some doubt[24] as to whether the dissociation rate constants derived from shock tube measurements at high temperature can be combined with equilibrium data to give true recombination constants. As the experimental dissociation rate constants are likely to be smaller[25] than the "equilibrium" values, the temperature dependence of the recombination reaction is exaggerated when the low temperature results are combined with data derived from the high temperature dissociation results. For this reason only results obtained for the direct recombination have been considered in this paper. The dissociation rate constants derived from the recombination rate constants and equilibrium data must refer to dissociation from the upper vibrational levels of the diatomic molecule. The high pre-exponential factor may be explained[26] in part, at least, by the concen-

---

(21) M. R. Basila, quoted from ref. 8.

(22) M. I. Christie, R. S. Roy and B. A. Thrush, *Trans. Faraday Soc.*, **55**, 1139 (1959).

(23) H. B. Palmer and D. F. Hornig, *J. Chem. Phys.*, **26**, 98 (1957).

(24) H. O. Pritchard, *J. Phys. Chem.*, **65**, 504 (1961).

(25) E. E. Nikitin and N. D. Sokolov, *J. Chem. Phys.*, **31**, 1371 (1959).

(26) O. K. Rice, *ibid.*, **9**, 258 (1941).

tration of vibrational levels in this region. Collision theory calculations show that mechanism A cannot explain values of recombination constants much higher than the values for the rare gases, even if a transfer of energy (reaction 4) occurred at every collision. The only significant contribution an energy transfer step involving degrees of freedom other than translational could make would be in connection with reaction 6; *i.e.*, the energy transfer theory can only be of importance if the complex mechanism C is in operation.

It cannot be claimed that the exact mechanism of recombination is known for any one system. The most plausible conclusion is that mechanisms B and C only are important and that the contribution of mechanism C probably increases with k_M. A possible explanation for the importance of mechanism B compared with mechanism A even for the rare gases may be that the field of M is more effective in the former case in weakening the selection rules which account for the theoretical statistical factor of $^1/_{16}$. The similarities between iodine and bromine atom recombination emphasize the fact that it is the intermolecular force field of the third body which is the main factor in determining the recombination rate constant, and that specific chemical interaction between atom and third body molecule is not involved.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA]

Physical Adsorption in the Multilayer Region on Heterogeneous and Homogeneous Surfaces

BY CONWAY PIERCE AND BLAND EWING

RECEIVED MAY 21, 1962

Adsorption isotherms for a very uniform surface graphite, Sterling MT (3100°) are compared with those for less uniform surfaces. The isotherm of ethyl chloride on MT at −78° gives a well defined second layer step, as predicted by the Frenkel–Halsey–Hill equation, $-\ln p/p_0 = k/\theta^s$, but nitrogen at −195°, ethyl chloride at 0°, benzene at 20° and *n*-hexane at 20° do not show this step. Reasons are discussed for the differences. When there is normal free surface adsorption a log–log plot of amount adsorbed *vs.* log p_0/p is linear throughout the multilayer region for all isotherms except those with steps. Applications of such plots are made for several types of isotherms and interpretations are given. It is shown that customary BET nitrogen areas for uniform surface graphites are in error, being about 80% of the true value. The reason is loose packing of N_2 molecules at the inflection point marking the start of multilayer adsorption. The isotherm becomes normal above a relative pressure of 0.4.

Physical adsorption in the region up to completion of the first layer and slightly beyond is well described by the BET equation[1] when the surface is heterogeneous. This equation also fits isotherms on uniform surfaces when the lateral interaction forces are small, but when they are large and the surface is highly uniform the isotherm is convex to the pressure axis up to near completion of the first layer (as shown in the ethyl chloride isotherm of Fig. 2) and the BET equation does not apply until past the convex region. Isotherms of this shape may be described by an equation developed by Kiselev and associates,[2] which takes the lateral interaction forces into account.

Neither the BET nor the Kiselev equation will fit experimental isotherms far into the multilayer region. As shown previously[3] this region is well described for many isotherms by the equation

$$-\ln p/p_0 = k/\theta^s \qquad (1)$$

where k is a constant related to the energy of adsorption in the first layer, θ is the number of statistical layers and the exponent s is related to the fall-off of the van der Waals forces of the surface with successive layers in the adsorbed film. This multilayer equation was developed independently by Frenkel,[4] Halsey[5] and Hill.[6] It has the advantage of giving a linear isotherm when the amount adsorbed is plotted *vs.* log p_0/p on a log–log scale. Deviations from a linear plot are useful for detection of capillary condensation.[3] These results have led to further study of the FHH equation for multilayer adsorption on both heterogeneous and homogeneous surfaces.

Experimental

Isotherms have been determined for nitrogen at −195° and ethyl chloride at 0 and −78° for two types of surfaces, an anatase from the lot used by Jura and Harkins[7] and a graphitized carbon black from Cabot[8] designated Sterling MT (3100°). The anatase has a heterogeneous surface and the graphite one of the most homogeneous surfaces yet described.

The adsorption line, shown in Fig. 1, is designed to cover a wide range of pressures, for vapors whose p_0 varies from 2 mm. to one atm. It is conventional in principle but embodies several features which are found to facilitate ease and accuracy of operation.

---

(1) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

(2) A. A. Isirikyan and A. V. Kiselev, *J. Phys. Chem.*, **65**, 601 (1961); **66**, 205, 210 (1962). References are given to more extended treatment in the original Russian publications.

(3) C. Pierce, *J. Phys. Chem.*, **64**, 1184 (1960); **63**, 1076 (1959).

(4) J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, New York, N. Y., 1946.

(5) G. D. Halsey, Jr., *J. Chem. Phys.*, **16**, 93 (1948); *J. Am. Chem. Soc.*, **73**, 2693 (1951); **74**, 1082 (1952). See also *Can. J. Chem.*, **33**, 184 (1955); *J. Phys. Chem.*, **57**, 646 (1953); **58**, 1011 (1954); **61**, 1158 (1957).

(6) T. L. Hill, "Advances in Catalysis," Academic Press, New York, N. Y., 1952; *J. Chem. Phys.*, **14**, 264, 441 (1946); **15**, 767 (1947); **17**, 580, 668 (1949).

(7) G. Jura and W. D. Harkins, *J. Am. Chem. Soc.*, **66**, 1146 (1941).

(8) Provided by Prof. J. M. Holmes, Carleton University, Ottawa, Canada. See J. M. Holmes and R. A. Beebe, *J. Phys. Chem.*, **61**, 1684 (1957). Our sample appears to be from the lot used by Isirikyan and Kiselev, which they designate MT-1. Below $0.4p_0$ our data coincide with their isotherm. Above this pressure we obtain slightly higher adsorption than they, but in this region they show no data for MT-1. The deviation is probably due to experimental uncertainty in dead space measurement, as discussed later. Further investigation will be made of this.