The Rate of Adsorption of Phosgene and Chloropicrin on Charcoal

Malcolm Dole

Articles you may be interested in

Comparison of phosgene formation from adsorption of carbon tetrachloride on oxygen modified Ir(111) and oxygen modified Ir(110)
J. Vac. Sci. Technol. A **19**, 1524 (2001); 10.1116/1.1366700

Surface Heterogeneity of a Charcoal: Comparison of Results of NMR and Adsorption Methods
J. Chem. Phys. **47**, 3685 (1967); 10.1063/1.1712453

Removal of Tritium from 3He by Adsorption on Charcoal
Rev. Sci. Instrum. **36**, 1250 (1965); 10.1063/1.1719856

Application of ChargeTransfer Theory to the Heats of Adsorption of the Inert Gases on Charcoal
J. Chem. Phys. **29**, 724 (1958); 10.1063/1.1744582

Adsorption Isotherms for HydrogenBonded Liquids on Charcoal
J. Chem. Phys. **14**, 642 (1946); 10.1063/1.1724079

The Rate of Adsorption of Phosgene and Chloropicrin on Charcoal

MALCOLM DOLE

Department of Chemistry, Northwestern University, Evanston, Illinois

(Received January 30, 1947)

Making use of a relationship between the adsorption rate constant and the maximum slope of the effluent concentration-time curves derived from the rate equation of Bohart and Adams, it has been possible to estimate an absolute rate of adsorption of phosgene and chloropicrin on charcoal from the experimental data of Dole and Klotz. It is shown that diffusion to the most accessible part of the charcoal surface will occur faster than the observed rate, but more slowly to the least accessible surface areas. Calculated rates of adsorption using the statistical equations of Glasstone, Laidler, and Eyring and of Temkin are also of the correct order of magnitude when plausible assumptions are made concerning the nature of the activated state. It is concluded that both diffusion and surface reaction mechanisms must be postulated to gain a complete understanding of the adsorption rate of the two gases, but with diffusion being less important in the case of phosgene.

INTRODUCTION

RELIABLE data for the rate of adsorption of gases on surfaces of known area have in the past been extremely scanty, but with the development of improved methods of obtaining significant information concerning the surface area of adsorbents and catalysts more rate data should become available. Because of extensive work done under the auspices of the OSRD on activated charcoal it has been possible for us to estimate from our data and the data of others experimental rate values for the adsorption of phosgene and chloropicrin. These estimated rates come from a study of effluent concentration-time .curves and are significant to the extent that the theory on which the estimates are based is significant as explained below. Chemical engineers have been active and successful in inventing empirical functions which describe the data, but there has been no attempt, as far as we know, to relate these chemical engineering functions to absolute reaction rate theories.

The rates given in this paper refer to the rate on charcoal which is in equilibrium with air; possibly, the initial displacement of adsorbed air molecules by the adsorbate may complicate the interpretation of the data as was, indeed, pointed out many years ago by Harned.[1] It would be interesting to repeat the measurements of Dole and Klotz using helium as the carrier gas. Emmett

and Cines[2] have shown that previous chemisorption of hydrogen does not in general reduce the adsorption area of nitrogen except for possible cases where the chemisorbed gas may block the smallest pores of the adsorbent. Perhaps this latter phenomenon was present in Harned's case as his charcoal had only about $\frac{2}{3}$ of the adsorptive capacity of ours.

DETERMINATION OF RATE CONSTANT

In our experimental work[3] gas at influent concentration c_0 in p.p.m. by volume was passed through a granular charcoal bed of length x cm,
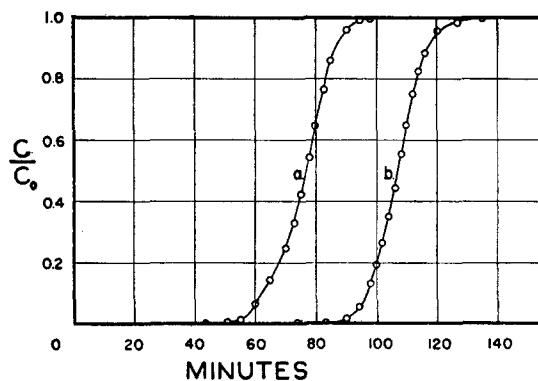

FIG. 1. Effluent to influent concentration-time curves. Curve a: chloropicrin at 7900 p.p.m., 62 liters/hour flow rate. Curve b: phosgene at 1760 p.p.m., 62 liters/hour flow rate.

[1] H. S. Harned, J. Am. Chem. Soc. 42, 372 (1920).

[2] P. H. Emmett and M. Cines, J. Am. Chem. Soc. 68, 2535 (1946).

[3] M. Dole and I. M. Klotz, Ind. Eng. Chem. 38, 1289 (1946); I. M. Klotz and M. Dole, Ind. Eng. Chem. Anal. Edition 18, 741 (1946).

of cross-sectional area A squared cm, at a flow rate L cc per sec., at 25°C, and under conditions such that the effluent concentration c could be measured at minute intervals. This effluent concentration which is a function of time, flow rate, initial concentration, length and area of bed, mesh size of charcoal, and temperature is illustrated in the case of two typical experiments on chloropicrin and phosgene in Fig. 1 where c/c_0, the ratio of effluent to influent concentration, is plotted as a function of time. For a tabulation of the more important data used in our calculations, see Appendix.

Bohart and Adams[4] have developed an adsorption rate theory assuming that the rate of adsorption, $\partial n/\partial t$, is proportional to the instantaneous concentration, c, (in this case of the gas in contact with the charcoal) and to the available

FIG. 2. Test of the Bohart-Adams adsorption rate equation. Curve a: chlorpicrin. Curve b: phosgene.

[4] G. S. Bohart and E. Q. Adams, J. Am. Chem. Soc. **42**, 523 (1920). For a review of adsorption rate theories see the paper by I. M. Klotz, *Chem. Rev.* **39**, 241 (1946), and S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943), Chapter XIII.

free surface of the charcoal, $n_0 - n$, or

$$\partial n/\partial t = k \cdot c(n_0 - n). \qquad (1a)$$

In our calculations n will be given in units of number of adsorbing sites which are occupied per sq. cm, (when n is used in connection with Eq. (1b) or (2) it should be expressed in units of no. per cc) t in sec., c in molecules per cc, n_0 represents the total number of adsorbing sites per sq. cm, occupied or unoccupied. Related to (1a) is the equation

$$\partial c/\partial x = -(k/u)c(n_0 - n), \qquad (1b)$$

which expresses the rate of change of concentration with distance.

On integration the following equation is obtained:[5]

$$\ln[(c_0/c) - 1] = \ln[\exp[kn_0(x/u)] - 1] - kc_0 t, \quad (2)$$

where u, in cm per sec., when given by L/A is the linear velocity of the gas-air stream in the adsorbent tube when empty. For the actual linear velocity between granules, L/A must be divided by the fraction of void space in the charcoal bed. For constant velocity of flow and constant input concentration, the effluent concentration, c, should be the following function of the time:

$$\log[(c_0/c) - 1] = \text{con} - (kc_0 t/2.303). \qquad (3)$$

Thus a plot of $\log[c_0/c - 1]$ against the time should give a straight line if this formulation is correct. In Fig. 2 we have plotted the data of Fig. 1 for both phosgene and chloropicrin according to the relationship expressed by Eq. (3). The phosgene data agree with Eq. (3) somewhat better than do the chloropicrin data.

Differentiating Eq. (2) with respect to time we obtain

$$\partial(c/c_0)/\partial t = k[c - (c^2/c_0)]. \qquad (4)$$

At the moment when $c/c_0 = 0.5$, the rate of rise of effluent concentration with time is a maximum; thus, at this point there should be an inflection point in the curve with slope given according to the theory by the equation

$$[\partial(c/c_0)/\partial t]_{c/c_0 = 0.5} = kc_0/4 = S_{\max}. \qquad (5)$$

[5] A similar treatment has recently been given by Danby, Davoud, Everett, Hinshelwood, and Lodge, J. Chem. Soc. 918 (1946).

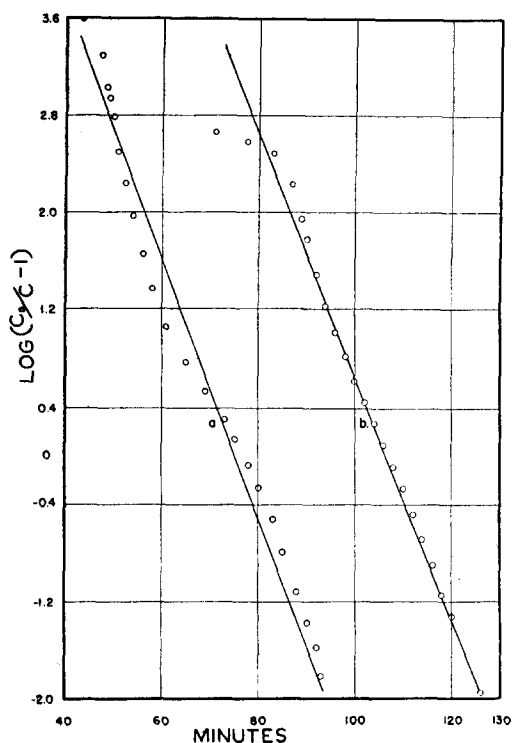In Fig. 3 a number of observed maximum slopes of the $c/c_0 - t$ curves, S_{max}, are plotted as a function of the influent concentration. A linear relation, extrapolating to the origin in accordance with the theory, is observed.

However, the situation is complicated by the influence of flow rate on S_{max} in contradiction to Eq. (5), particularly in the case of chloropicrin. Variation in particle size will also probably produce a slight change in S_{max}, although we have no data to test this point. Figure 4 illustrates the variation of S_{max} with flow rate. Unfortunately the OSRD sponsored research did not include a comprehensive study of the variation of S_{max} with particle size and flow rate, but the data of Fig. 4 show that the phosgene S_{max} values are affected only slightly by the change of flow rate, but the chloropicrin S_{max} data somewhat more so. As a first approximation we shall assume that the slopes of the straight lines of Fig. 3 correctly give the value of $k/4$ for the two gases; at any particular concentration, then, k can be calculated from the equation

$$k = 4S_{max}/c_0. \qquad (6)$$

The rate constant, k, can be estimated also from the slopes of the curves of Fig. 2; when so determined there is fairly good agreement with the value of k given by the method used here in the case of phosgene, whose data follow the integrated Eq. (3) relationship much better than do the chloropicrin data. The rate constant for this latter gas may vary as much as 75 percent depending on which part of the curve of Fig. 2 is used in computing the slope. However, we have not used the slopes of the curves of Fig. 2 for either chloropicrin or phosgene in calculating k because the slopes so determined do not vary as nearly linearly with the concentration, and do not extrapolate as well to zero at zero concentration as do the points of Fig. 3. For this reason we believe that the k values determined from the linear curves of Fig. 3 are somewhat more significant.

For the calculation of the absolute reaction rate from the rate constant of Eq. (6) it is necessary to know the surface area available for adsorption per gram of charcoal. Emmett and co-workers[6] have determined the surface area of the

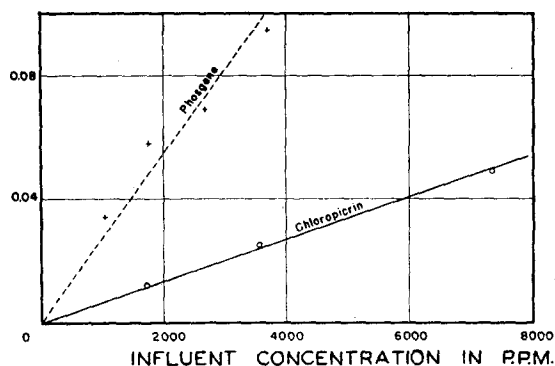[6] P. H. Emmett et. al., Private communication.

FIG. 3. Test of Eq. (5).

charcoal we used for nitrogen, chloropicrin, and a number of other gases, but not phosgene. For the latter we have chosen a reasonable estimate which is undoubtedly of the correct order of magnitude. Knowing k and n_0, the actual absolute rate, $\partial n/\partial t$ can be calculated from Eq. (1) for any chosen values of c and $n_0 - n$. In Table I the maximum rate of adsorption, which would be a rate at zero time when c equals c_0, and $n_0 - n$ equals n_0, is tabulated along with other related data. Such a rate could only be produced experimentally at x equal to zero.

THE ROLE OF DIFFUSION

Before proceeding to consideration of the interpretation of the data on the basis of an absolute reaction rate theory, it is interesting to
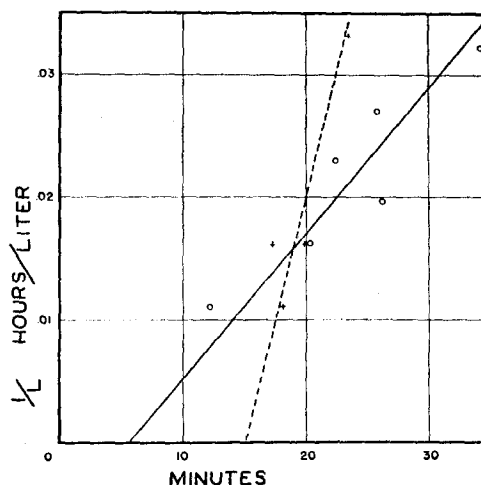

FIG. 4. Variation of adsorption rate constant with flow rate. Circles: chloropicrin. Crosses: phosgene. Abscissa is reciprocal of S_{max}.

TABLE I. Adsorption data for chloropicrin and phosgene on activated charcoal at 25°C.

Gas	Area of adsorbent cm^2 g^{-1}	k cm^3 molecules^{-1} sec.$^{-1}$	c_0 molecules cm^{-3}	n_0 sites cm^{-2}	Maximum rate of adsorption molecules cm^{-2} sec.$^{-1}$
Chloropicrin	1.13×10^7	1.89×10^{-20}	1.93×10^{17}	2.9×10^{14}	1.06×10^{12}
Phosgene	1.5×10^7	7.62×10^{-20}	4.34×10^{16}	3.42×10^{13}	1.13×10^{11}

consider the possible role of diffusion as the rate-controlling mechanism. For the simplest case of diffusion across a plane surface layer of unit area and thickness δ, and with a concentration difference equal to c_0, the rate is given by the equation

$$v = Dc_0/\delta, \tag{7}$$

where D is the diffusion coefficient of the gas in air.

To apply Eq. (7) which should be valid for the calculation of the maximum rate of adsorption because at the first moment of adsorption the concentration of gas right at the charcoal surface will be effectively zero, we need to know the length of path and the area through which diffusion is taking place. Gamson, Thodos, and Hougen[7] give a table of effective area of mass transfer for particles of different mesh sizes. In our case of 12–14 mesh particles having 45 percent void space (bulk density equal to 0.48), the gross surface area of the particles is 792 sq. ft. per cubic ft. of volume or 54.1 sq. cm per g. The charcoal granule itself contains many pores having a distribution of sizes; roughly 45 percent by volume of the granule is made up of pores whose diameters are not much greater than that of the chloropicrin molecule. (The 45 percent void space is not to be confused with the 45 percent volume of small pores in the granule.) The diameters of most of these pores are, therefore, much smaller than the mean free path of air molecules at atmospheric pressure; hence, each small hole in the charcoal should act as a "trap" for a chloropicrin molecule. Every chloropicrin molecule initially striking one of these holes from the flowing air stream should be adsorbed if the adsorption process takes place on every collision of a chloropicrin molecule with the surface. In other words, nearly every chloropicrin molecule

striking one of these holes must collide with the charcoal surface before it diffuses out of the hole.

From the kinetic theory of gases or from the absolute reaction rate theory of Eyring and co-workers, the rate at which molecules strike unit area of surface per sec. is given by the following equation:[8]

$$v = c_0 [kT/2\pi m]^{\frac{1}{2}}. \tag{8}$$

For chloropicrin at $c_0 = 1.93 \times 10^{17}$ molecules/cm^3

$$v = 9.47 \times 10^{20} \text{ molecules/cm}^2/\text{sec.},$$

and for phosgene at $c_0 = 4.34 \times 10^{16}$ molecules/cm^3

$$v = 2.75 \times 10^{20} \text{ molecules/cm}^2/\text{sec.}$$

However, the above calculations refer to the rate at which molecules would be striking unit area; for an area of 45 percent of 54 cm^2 per gram, the rates become

2.30 × 10^{22} molecules/gram/sec. for chloropicrin, and
6.68 × 10^{21} molecules/gram/sec. for phosgene.

The observed rates are

1.20 × 10^{19} molecules/gram/sec. for chloropicrin, and
1.60 × 10^{18} molecules/gram/sec. for phosgene

which is about 2000 times smaller than was calculated. Apparently there must be many molecules which diffuse out of the holes without being adsorbed.

We shall now consider the rate at which molecules can diffuse into the granule through the pores, but the validity of our calculations will be somewhat in doubt because we do not know the complete details of the pore structure of the charcoal granules or the true diffusion rates in the pores. Apparently the pores can be divided roughly into two groups; macropores with diameter of the order of 10^{-4} cm and micropores whose diameters lie between 10^{-7} and 10^{-6} cm.[9] We shall assume that the diffusion constants for diffusion through the macropores are equal to those for diffusion in air, which as determined in this laboratory for chloropicrin and phosgene are, respectively, 0.088 and 0.099 cm^2/sec. For diffusion in the micropores we make use of the diffusion

[7] B. W. Gamson, G. Thodos, and D. A. Hougen, Trans. Am. Inst. Chem. Eng. **39**, 1 (1943).

[8] See S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, New York, 1941), p. 351.
[9] See S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943).

constant calculated from the following equation[9] derived for uni-dimensional gaseous diffusion through a cylindrical pore,

$$D_i = \tfrac{2}{3}r(8RT/M)^{\frac{1}{2}},$$

where r is the radius of the pore. Surface diffusion will not be considered because we are dealing with the rate of adsorption at zero time when the charcoal is free of adsorbate. The micropore diffusion constants as calculated for chloropicrin and phosgene are, respectively, 1.17×10^{-3} and 1.52×10^{-3} cm²/sec., for r approximately 10^{-7} cm.

The average radius of the charcoal granules of 12–14 mesh, again taken from Gamson, Thodos, and Hougen, is 0.0635 cm. From Eq. (7) we can calculate that the rate of diffusion through a concentration gradient equal to c_0, through an area of 45 percent of 54 cm² per grams, and along a distance of 0.0635 cm is

$v = 8.7 \times 10^{16}$ molecules/gram/sec. for chloropicrin, and
$v = 2.57 \times 10^{16}$ molecules/gram/sec. for phosgene,

about 100 times slower than was observed. For diffusion through the macropores the calculated rate is

$v = 2.02 \times 10^{18}$ molecules/gram/sec. for chloropicrin, and
$v = 5.11 \times 10^{17}$ molecules/gram/sec. for phosgene,

which is within an order of magnitude of the observed rates. For distances of diffusion shorter than 0.0635 cm the rate would be faster than that observed.

This calculation suggests that diffusion to the most readily accessible areas of the charcoal where δ is much smaller than 0.0635 cm can proceed faster through the large pores than the observed initial adsorption rate. At later stages of the process where the gas has to diffuse through small pores to reach unused charcoal surface, the diffusion rate would be slower and perhaps rate determining. If this is true, the asymmetric shape of the effluent concentration-time curves and the influence of flow velocity on the rate can be at least partially understood. However, it should be emphasized that these calculations are not sufficiently exact for the possibility of a diffusion-controlling mechanism to be definitely excluded. Agreement of the data with Eq. (3) also does not definitely exclude the

possibility that the magnitude of the constant k is determined by diffusion, but any diffusion theory will have to explain the fourfold greater value of k for phosgene as compared to chloropicrin which it cannot do if only diffusion through air is considered.

The question naturally arises as to whether diffusion from the moving air stream to the gross surface of the charcoal is the limiting factor. Although this diffusion probably determines in large part the "critical bed depth" we do not believe that it is entirely responsible for the adsorption rate as given above for the following reasons: (a) if diffusion from the moving gas stream is determinative, the S_{max} slopes should be independent of initial concentration and greatly dependent on the flow rate[10] whereas the reverse is true; (b) the rate constants, k, for chloropicrin and phosgene should be nearly equal because of their nearly equal diffusion coefficients, but the observed rate constant for phosgene is four times that for chloropicrin.

We shall now investigate the extent to which the absolute surface reaction rate theory can explain the observed values.

APPLICATION OF THE ABSOLUTE REACTION RATE THEORY

In order to apply the equation derived by Laidler, Glasstone, and Eyring,[11] and Temkin[12] to the interpretation of the reaction rate constants it is necessary to know the moments of inertia of the chloropicrin and phosgene molecules. In the case of chloropicrin we have made use of the following bond distances and bond angles:

C−N	1.47A
C−Cl	1.77A
N=O	1.21A
Angle Cl−C−Cl	111°
Angle O−N−O	127°

Assuming free rotation about the C−N bond, the equations for the separate moments of inertia

[10] This follows from the diffusion theory of C. C. Furnas, Trans. Am. Inst. Chem. Eng. **24**, 1942 (1930).
[11] K. J. Laidler, S. Glasstone, and H. Eyring, J. Chem. Phys. **8**, 659 (1940); *The Theory of Rate Processes* (McGraw-Hill Book Company, New York, 1941), Chapt. VII.
[12] M. Temkin, Acta Physicochim. U.R.S.S. **8**, 141 1938).

have been set up as follows:

$$I_x = 2m_O\left(r_{N-O}\,\sin\frac{127°}{2}\right)^2$$

$$+3m_{Cl}\left(r_{C-Cl}\frac{\sin(111°/2)}{\sin60°}\right)^2$$

$$= 5.64\times10^{-38}\ \text{g cm}^2,$$

$$I_y = I_z = 3m_{Cl}$$

$$\times\left[r_x+r_{C-Cl}\left(1-\left(\frac{\sin(111°/2)}{\sin60°}\right)^2\right)^{\frac{1}{2}}\right]^2 \quad (9)$$

$$+\tfrac{3}{2}m_{Cl}\left[r_{C-Cl}\frac{\sin(111°/2)}{\sin60°}\right]^2$$

$$+m_C r_x{}^2+m_N[r_{C-N}-r_x]^2$$

$$+2m_O[r_{C-N}-r_x+r_{N-O}\cos(127°/2)]^2$$

$$+m_O[r_{N-O}\sin(127°/2)]^2,$$

where

$$r_x = \left[m_N\cdot r_{C-N}+2m_O(r_{C-N}+r_{NO}\cos(127/2))\right.$$

$$-3m_{Cl}\cdot r_{C-Cl}$$

$$\left.\times\left(1-\left(\frac{\sin(111°/2)}{\sin60°}\right)^2\right)^{\frac{1}{2}}\right]\Big/ m_{CCl_3NO_2}$$

$$= 0.16\text{A}. \quad (10)$$

Hence, $I_y = I_z = 5.92\times10^{-38}$ g cm². (If free rotation is not assumed, $I_y \neq I_z$, but the product $I_y I_z$ remains unchanged, which is all that concerns us here). The simpler calculations of the moments of inertia of phosgene yielded the results

$$I_x = A = 1.81\times10^{-38}\ \text{g cm}^2,$$
$$I_y = B = 1.72\times10^{-38},$$
$$I_z = A+B = C = 3.53\times10^{-38}.$$

As we shall assume that the vibrational partition function ratio in the free and adsorbed states is unity, we do not need to consider vibration frequencies.

The general equation for the rate of adsorption is, in the symbolism of Glasstone, Laidler, and Eyring

$$v = c_g\cdot c_s\frac{kT}{h}\cdot\frac{f_{\ddagger}}{F_g f_s}\exp\left[-\frac{\epsilon}{kT}\right], \quad (11)$$

where c_g is the gas concentration in molecules per cc, c_s the number of adsorbing points per sq. cm., $f_{\ddagger}$ the partition function of the activated complex (with the contribution of the degree of translational freedom normal to the adsorbing surface factored out), F_g the partition function per unit volume of the gas undergoing adsorption, f_s the partition function of the adsorbing centers (taken as unity) and ϵ is the activation energy for adsorption per molecule at the absolute zero. The maximum rate of adsorption given by Eq. (1) when the concentration is equal to the influent concentration and the surface is bare can be expressed by the equation

$$v = k\cdot c_g\cdot c_s. \quad (12)$$

Combining Eqs. (11) and (12)

$$k = \frac{kT}{h}\frac{f_{\ddagger}}{F_g}e^{-\epsilon/kT}. \quad (13)$$

Remembering that k can be calculated from Eq. (6) without a knowledge of n_0, it is seen that the absolute theory of reaction rates can be tested without knowing either the surface area of the adsorbent or the number of adsorbing centers per sq. cm. Only the validity of Eq. (6) is required.

In applying Eq. (13) three cases have been tested; first, the case in which the adsorbate loses its translational degrees of freedom in the activated complex (except in the direction required for adsorption); second, the adsorbate loses its translational and two of its rotational degrees of freedom; and third, the adsorbate becomes completely immobile losing all translational and rotational degrees of freedom. Equations for k based on these assumptions are as follows:[13]

Case 1.

$$k = \left[h^2/(2\pi m)^{\frac{1}{2}}(kT)^{\frac{1}{2}}\right]\exp\left[-(\epsilon/kT)\right]. \quad (14)$$

Case 2.

$$k = (\sigma/\sigma_{\ddagger})$$

$$\times\left[h^4/8\pi^2(BC)^{\frac{1}{2}}(2\pi mkT)^{\frac{1}{2}}\right]\exp\left[-\epsilon/kT\right]. \quad (15)$$

[13] The equation given for the rate of a heterogeneous unimolecular first-order reaction involving a nonlinear polyatomic molecule by Glasstone, Laidler, and Eyring, reference 11, should be divided by a factor $(kT)^{\frac{1}{2}}$.

Case 3.

$$k = (\sigma/\sigma_{\ddagger})[h^5/(2\pi m)^{\frac{3}{2}}8\pi^2(8\pi^3 ABC)^{\frac{1}{2}}(kT)^2]$$

$$\times \exp[-\epsilon/kT]. \quad (16)$$

In Table II values of k calculated from (14)–(16), assuming zero activation energy, are given along with ratios of k for the two gases and other pertinent data.

Before coming to any conclusions as to the validity of the theory, it is important to consider the effect of activation energy and change of temperature on the rate constants. By inspection of Eqs. (14)–(16) it can be seen that if the activation energy is really zero, the rate constants should decrease with rise of temperature; if there is no temperature dependence of the rate constant, it may be because the increase of the factor $\exp[-\epsilon/kT]$ with increase of the temperature has balanced the decrease of the terms $(kT)^{-\frac{1}{2}}$, $(kT)^{-\frac{1}{2}}$, or $(kT)^{-2}$ over the temperature interval from 0 to 25°C.

Unfortunately only one rate experiment was carried out at 0°C from which the activation energy could be calculated; hence, the exact value of the rate constant at 0°C given in Table II is uncertain. We believe that the change in k over the 25°C temperature interval would be no greater than that indicated in Table II.

If allowance is made for the variation in k because of the kT factors of Eqs. (14), (15), and (16), the values of E necessary to explain the observed change in k with temperature, given in the last column of Table II, are obtained; recalculating the rate constants by Eqs. (14), (15), and (16) by use of these values of the activation energy, the values given in the next to the last column result.

Whether an activation energy exists or not, it is obvious that the absolute reaction rate theory can reproduce the observed data depending on the assumptions as to the status of the adsorbed chloropicrin and phosgene molecules in the activated state.

CONCLUSIONS

In conclusion we believe that our calculations demonstrate that both the diffusion and surface reaction mechanisms of adsorption are involved in the actual adsorption process. As explained in

TABLE II. Comparison of experimental and theoretical adsorption rate constants.

	Chloropicrin Phosgene (k in cm^3 sec^{-1} at 25°C)		Ratio	k, chloropicrin temp. corrected	E cal./ mole
k, obs. 25°	1.89×10^{-20}	7.62×10^{-20}	4.03		
k, obs. 0°	1.17×10^{-20}				
k, Eq. (14)	3.06×10^{-16}	6.52×10^{-16}	2.13	7.83×10^{-16}	3500
k, Eq. (15)	6.99×10^{-19}	3.57×10^{-18}	5.10	6.89×10^{-22}	4100
k, Eq. (16)	6.09×10^{-21}	5.51×10^{-20}	9.05	3.79×10^{-24}	4400

the previous paper of Dole and Klotz the diffusion theory alone is inadequate because (1) the critical bed depths do not extrapolate to zero for zero particle diameter, (2) the maximum slope of the effluent concentration-time curve is so strongly dependent upon the concentration, and (3) the rate constant for phosgene is four times as great as that for chloropicrin, although the diffusion constant of phosgene is only slightly greater than that of chloropicrin. It should be noted that we have not postulated any condensed surface film of gas through which diffusion at a slower rate must take place; however, the influence of flow velocity on the rate is to be considered as an increase of net rate of transfer of gas to the charcoal surface with increased flow velocity.

The difficulty of expressing the rate of adsorption by a single equation undoubtedly stems from the mixture of mechanisms entering into the adsorption process.

Danby, Davoud, Everett, Hinshelwood, and Lodge[5] have recently carried out an experimental and theoretical analysis of adsorption rates similar to that of Dole and Klotz. They believe that the adsorption of chloropicrin is diffusion controlled because their adsorption rate constants are proportional to the square root of the flow rate, and inversely proportional to the square root of the molecular weight (the latter because of an assumed proportionality between the diffusion constant and the square root of the molecular weight). These relationships are not verified in our work and, in fact, the diffusion coefficients of gases in air do not follow the square root of molecular-weight law. Unfortunately we did not study effluent concentration-time curves as a function of particle size, hence we cannot comment on their suggestion that n_0 is a decreasing linear function of the particle diameter.

APPENDIX

MALCOLM DOLE AND I. M. KLOTZ

Experimental Data from Which Figs. 1, 2, and 3 Were Constructed[14]

Chloropicrin. (Bed depth 5.3 cm, diameter 1.4 cm, and temperature 25°C except where otherwise specified.)

Exp. 15, c_0, 7900 p.p.m. Flow rate 62 liters/hour. Bed depth 6.3 cm				Exp. 17, c_0, 7350 p.p.m. Flow rate 62 liters/hour			
Time min.	c/c_0	Time min.	c/c_0	Time min.	c/c_0	Time min.	c/c_0
43.5	0.0003	71	.273	36	0.0003	59	.235
47.5	.0005	72	.303	38	.0004	60	.267
48.5	.0009	73	.332	39	.0015	61	.299
49	.0011	74	.366	40	.0025	62	.338
50	.0020	75	.423	41	.0037	63	.374
51	.0032	76	.463	42	.0054	64	.418
52.5	.0057	78	.544	43	.0079	65	.476
53	.0068	79	.600	44	.0113	67	.553
54	.0104	80	.646	45	.0159	68	.607
55	.0158	81	.686	46	.0219	69	.653
56	.0216	82	.731	47	.0290	70	.717
57	.0295	83	.768	48	.0376	71	.769
58	.0399	84	.819	49	.0474	72	.817
59	.0512	85	.861	50	.0543	73	.857
60	.0647	86	.886	51	.0709	74	.897
61	.0800	87	.910	52	.0845	75	.917
62	.0952	88	.930	53	.1000	76	.953
63	.112	89	.950	54	.113	77	.969
64	.129	90	.960	55	.136	78	.979
65	.145	91	.970	56	.157	79	.984
66	.163	92	.975	57	.179	80	.995
67	.182	93	.985	58	.204	84	1.000
68	.202	94	.990				
69	.227	98	1.000				
70	.248						

Exp. 25, c_0, 3600 p.p.m. Flow rate 62 liters/hour		Exp. 30, c_0, 1740 p.p.m. Flow rate 62 liters/hour	
Time min.	c/c_0	Time min.	c/c_0
82.5	0.0006	156	0.0006
84	.0014	171	.0069
85	.0014	175	.0103
86	.0020	179	.0161
88	.0022	185	.0264
90	.0039	193	.0467
91	.0045	196	.0555
94	.0070	200	.0700
96	.0093	204	.0918
99	.0163	208	.106
103	.0334	212	.129
104	.0379	216	.155
106	.0497	220	.188
109	.0756	223	.216
114	.152	227	.253
115	.169	230	.287
116	.190	234	.338
118	.234	241	.432
120	.280	246	.498
121	.302	256	.609
123	.351	266	.720
125	.399	280	.870
127	.447	300	.98
129	.499	315	1.00
136	.689		
141	.809		
145	.885		
150	.981		
156	1.000		

Phosgene. (Bed depth, 5.0 cm, bed diameter 1.4 cm, and temp. 25°C except when otherwise stated.)

Exp. 1, c_0, 1790 p.p.m. Flow rate, 62 liters/hour		Exp. 4, c_0, 1800 p.p.m. Flow rate, 62 liters/hour. Bed depth, 10.0 cm	
Time min.	c/c_0	Time min.	c/c_0
36	0.0020		
38	.0026	71	0.0021
40	.0045	77.5	.0026
42	.0073	83	.0032
43	.0094	87	.0058
44	.0126	89	.0110
46	.0208	90	.0162
48	.0384	92	.0316
50	.0601	94	.0552
52	.0975	96	.0884
54	.1530	98	.1328
56	.2282	100	.1920
58	.3187	102	.2650
60.5	.4520	104	.3500
62	.5380	106	.4450
64	.6570	108	.5540
66	.7630	110	.6500
68	.8400	112	.7500
70	.8965	114	.8270
72.5	.9350	116	.8890
75	.9630	118	.9340
77	.9750	120	.9550
80	.9850	127	.9890
83	.9960	135	1.0000
85	1.0000		

Exp. 40, c_0, 3700 p.p.m. Flow rate 62 liters/hour		Exp. 42, c_0, 2700 p.p.m. Flow rate 62 liters/hour	
Time min.	c/c_0	Time min.	c/c_0
27.5	0.0010	28.5	0.0006
29.5	.0468	30.5	.0023
31	.1268	32.5	.0069
32.5	.1749	34	.0174
33	.2210	35	.0287
34.5	.3135	36	.0452
35	.3700	37	.0634
36	.4400	38	.0915
37	.5090	39.5	.1272
38	.5970	40.5	.1740
39.5	.7460	42	.3120
40.5	.7760	45	.4140
42	.8560	46	.5200
44.5	.9390	47.5	.5950
46.5	.9660	49	.6990
50.5	1.0000	50.5	.8050
		52	.8400
		53.5	.8810
		55	.9230
		57	.9530
		58	.9600
		64	.9790
		72	.9410
		83	.9910
		95	.9950
		113	1.0000

Exp. 43, c_0, 1060 p.p.m. Flow rate, 62 liters/hour	
Time min.	c/c_0
42.5	0.0014
45	.0025
46.5	.0065
50	.0127
53.5	.0196
57	.0330
63	.0723
69	.1240
73.5	.1520
79	.2900
88.5	.5620
98.5	.7980
114	.9030
192	1.0000

[14] Dole and Klotz, Ind. Eng. Chem. **38**, 1289 (1946).