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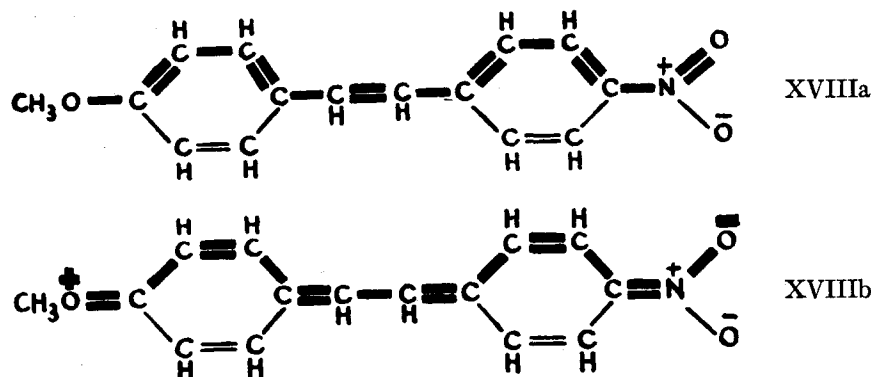
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The maximum shift that an auxochrom-antiauxochrom combination can cause would be achieved when the dipolar structure and the reference structure contribute each just 50 percent to the normal state.

This can be brought about by a suitable combination of the electron-donating property of the auxochrom and the electron-accepting tendency of the antiauxochrom, and is just realized in the case of the merocyanines XIIIa, XIIIb. In the case of the stilbene dye XVIII, however, the reference structure XVIIIa is markedly more predominant than the dipolar structure XVIIIb, as the absorption band is still found at far shorter wavelengths than would be expected on the basis of the free-electron gas model.

In the compound XIX the dipolar structure contributes relatively more than that of the dye XVIII just discussed. The dye XIX arises from XVIII when the auxochrom $-\text{OCH}_3$ is replaced by the stronger electron donor $-\text{NH}_2$, which thus enhances the im-

portance of the dipolar structure. It would then be expected that the absorption band of XIX will lie at longer wave-lengths than that of XVIII. This is also the case, as is shown by their red and yellow colors, respectively.

We have seen that a one-dimensional electron gas model leads to a quantitative explanation of the color of simple dye molecules. The success of the model in giving qualitative information about complex cases allows us to hope that a more general theory will be established on this basis which very likely would also be able to explain the color of inorganic complexes such as Prussian blue and molybdenum blue.

Acknowledgments: The author is grateful to Alexander Silberberg for his help in the preparation of the manuscript, to Professor Werner Kuhn for his interest in this work, and to the Ciba-Stiftung and Jacques-Brodbeck-Sandreuter-Stiftung for a grant.

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The Kinetics of Heterogeneous Atom and Radical Reactions. I. The Recombination of Hydrogen Atoms on Surfaces

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The data on the kinetics of the recombination of hydrogen atoms on various types of surfaces are analyzed in the light of the theory of absolute reaction rates. Expressions are derived for the recombination coefficient and the first-order rate constant, enabling these quantities to be calculated on the basis of postulated mechanisms. It is shown that the experimental activation energies are consistent with estimates using either Hirschfelder's rule or an expression utilizing the experimental "desorption temperature." For the reaction on dry oxides and dry glass good agreement is found assuming that reaction occurs between a gas-phase hydrogen

atom and an adsorbed hydrogen atom, the adsorption being of the van der Waals type at low temperatures and chemisorption at higher ones. The mechanism of surface poisoning by water vapor is shown to be not due to the necessity for desorbing the water molecule: in the high temperature region it is due to an increase in activation energy, the mechanism being $\text{S}-\text{OH}+\text{H}\rightarrow\text{S}-\text{O}+\text{H}_2$; in the low temperature region to a decrease in the number of active centers, the reaction being between a gaseous atom and a van der Waals adsorbed hydrogen atom above the water layer.

INTRODUCTION

THERE have now accumulated sufficient data on heterogeneous atomic and free radical recombinations to permit an analysis of the kinetics and a

discussion of possible reaction mechanisms. The work up to 1941 has been reviewed by L. von Müffling,¹ and an important investigation since then has been carried

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¹ L. von Müffling, in G. M. Schwab's *Handbuch der Katalyse* (Verlag Julius Springer, Berlin, 1943), Vol. VI, p. 94.

out by W. V. Smith.² Most of the data are on hydrogen atom recombination, and this work will be considered in the present paper; many of the conclusions arrived at are, however, applicable to recombinations of other types of atoms and radicals.

KINETIC MECHANISMS

All atom and radical recombinations on surfaces, whether poisoned or not, have been found to be of the first order over a wide range of temperatures, and it is necessary to consider what mechanisms will account for this. One that might be postulated is surface adsorption of the atoms (a first-order process), followed by migration and recombination on the wall; this is, however, excluded by M. C. Johnson's observation³ that hydrogen atoms may be packed tightly on a glass surface without recombination. An alternative mechanism, and by far the most probable one, is reaction between a surface-adsorbed atom and a gaseous atom. The observed first-order kinetics then require the fraction of surface covered by atoms to be independent of the atomic concentration in the gas phase, i.e., the surface must be fully covered. That this condition actually obtains in atomic adsorption has been shown directly by I. Langmuir.⁴ In a theoretical discussion of surface processes one of us⁵ has developed the kinetic laws applicable to both of the above mechanisms, and has shown on the basis of energy considerations why the second will almost invariably occur to the exclusion of the first.

THE RECOMBINATION COEFFICIENT

The fact that the order is the first implies that each gaseous atom arriving at the surface and reacting with an adsorbed atom has a certain constant reaction probability, which is independent of the pressure. One can therefore define a recombination coefficient γ , equal to the ratio of atoms striking the surface and reacting to the total number striking the surface; this coefficient is equivalent to the *Haftungskoeffizient* defined by F. A. Paneth and K. F. Herzfeld.⁶ The relationship between γ and the first-order rate constant k is readily obtained for a static system as follows. Consider a system of volume V cc containing n atoms reacting at a surface of S sq. cm. By the definition of k the number reacting per second is given by

$$-dn/dt = kn \text{ atom sec.}^{-1}, \quad (1)$$

while the number of atoms striking a surface of S cm² per second is given according to kinetic theory by

$$Z = (n\bar{v}/V4)S, \quad (2)$$

² W. V. Smith, J. Chem. Phys. 11, 110 (1943); thesis, Harvard University (1941).

³ M. C. Johnson, Trans. Faraday Soc. 28, 162 (1932).

⁴ I. Langmuir, J. Chem. Soc. 511 (1940).

⁵ K. J. Laidler, J. Phys. Chem. 53, 712 (1949).

⁶ F. A. Paneth and K. F. Herzfeld, Zeits. f. Elektrochemie 37, 577 (1931).

TABLE I. Experimental and estimated activation energies for atom recombinations.

Atom	Surface	T_d (°K)	$-\Delta H_{ads}$ (kcal.)	Activation energy (kcal.)		
				Experi- mental	Eq. (14)	Eq. (16)
H	Clean glass	500 ^a	10-11 ^b	0.9 ^c	1	0.6
H	Metals	1500 ^d	50-60 ^b	2.5-3 ^e	3	2.5-3.3
N	Nickel	1200-1350 ^f	55 ^f	2.5-3 ^f	2.4-2.7	3

^a M. C. Johnson, Trans. Faraday Soc. 28, 162 (1932).

^b See reference 1.

^c A. L. Robinson and I. Amdur, J. Am. Chem. Soc. 55, 2615 (1933).

^d See reference 4.

^e O. I. Leipunsky, Acta physicochimica, U.R.S.S. 5, 271 (1936).

^f N. Buben and A. Schechter, Acta physicochimica, U.R.S.S. 10, 371 (1939).

where \bar{v} is the mean atomic velocity. The recombination coefficient is the ratio of these quantities, i.e.,

$$\gamma = (4kV/\bar{v}S). \quad (3)$$

Usually the experiment is carried out in a cylindrical tube, so that $V = \pi r^2 L$ and $S = 2\pi r L$ where r is the radius and L is the length; in this case*

$$\gamma = (2kr)/\bar{v}. \quad (4)$$

This equation is identical with that derived by Paneth and Herzfeld⁶ for the case of a flow experiment involving an inert transport gas. It will be shown in the Appendix that this equation is also valid for a flow system where the transport of the atoms in a reaction tube is by diffusion alone. The experimental data quoted in this paper pertain to a system of this nature.

Expressions for k and γ will now be obtained using the theory of absolute reaction rates,⁷ and will be applied to the data in subsequent sections. The rate of a first-order surface reaction has been shown⁸ to be

$$v_1 = C_g C_s (kT/h) (f^\# / F_g f_s) e^{-E/RT}, \quad (5)$$

where C_g is the concentration of gaseous atoms, C_s the number per sq. cm of surface species with which reaction occurs, k is the Boltzmann constant, h is Planck's constant, $f^\#$ the partition function for the activated complex, f_s the partition function of the surface reactant and F_g that per unit volume of the reacting gas; E is the energy of activation of the process. This rate is related to the rate constants \bar{k} and k' by $v_1 = kC_g V/S = k' C_s$, whence

$$k' = C_s (kT/h) (f^\# / F_g f_s) e^{-E/RT}. \quad (6)$$

With the usual assumption that $f^\# / f_s = 1$ for an immobile layer, and evaluating the partition function F_g

* It may be noted that the appearance of r in this equation is due to the fact that k as ordinarily defined for a surface reaction (see Eq. (1)) is not a true constant but is inversely proportional to r ; the true heterogeneous first-order rate constant is $k' = kV/S$; γ on the other hand is a true constant.

⁷ H. Eyring, J. Chem. Phys. 3, 107 (1935); see Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

⁸ Laidler, Glasstone, and Eyring, J. Chem. Phys. 8, 659, 667 (1940).

for the gaseous atoms of mass m , Eq. (6) becomes

$$k' = C_s \frac{h^2}{(2\pi m)^{1/2} (kT)^{1/2} b_g} e^{-E/RT}, \quad (7)$$

where b_g represents the rotational and vibrational factors in the partition function of the gaseous reactants (unity in the case of atoms).

The recombination coefficient γ has been evaluated by Laidler⁵ using absolute rate theory, making use of the fact that the number of collisions on a surface is equivalent to the rate of adsorption to give a mobile layer when there is no activation energy for adsorption, namely,

$$\gamma = \frac{v_1(\text{immobile})}{v_1(\text{mobile})} \quad (8)$$

$$\gamma = \frac{C_s C_s (kT/h) (f^\ddagger/F_g f_s) \exp(-E/RT)}{C_g (kT/h) (F^\ddagger/F_g)}, \quad (9)$$

where F^\ddagger is the partition function for the activated complex in the mobile layer. Evaluation of the partition functions gives

$$\gamma = \frac{C_s h^2}{2\pi m k T b_g} e^{-E/RT}. \quad (10)$$

Expressions (7) and (10) for k' and γ may be seen to be consistent with Eq. (4) when it is noted that $\bar{v} = (8kT/\pi m)^{1/2}$.

THE ENERGY OF ACTIVATION

Equations (7) and (10) permit an absolute calculation of the first-order rate constant and the recombination coefficient provided that C_s and E are known. An approximate estimate of C_s can usually be obtained, but the energy of activation presents a little more difficulty. Two useful procedures are available. According to Hirschfelder⁹ the activation energy of an exothermic process $A + BC \rightarrow AB + C$ is given to a rough approximation by

$$E = 0.055 D_{BC}, \quad (11)$$

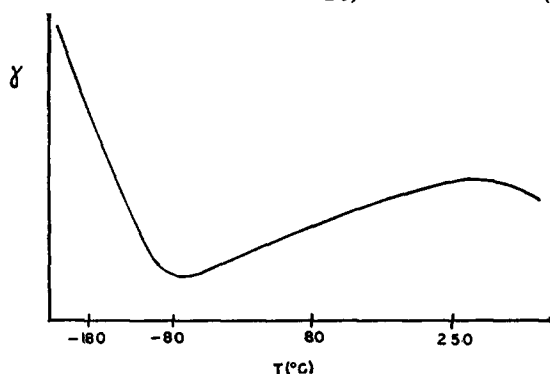


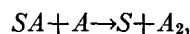
Fig. 1. Temperature variation of the recombination coefficient for hydrogen atoms on clean glass surfaces.

⁹ J. O. Hirschfelder, J. Chem. Phys. 9, 645 (1941).

where D_{BC} is the energy of dissociation of BC ; if the reaction is endothermic the energy of activation is

$$E = 0.055 D_{AB} + \Delta H, \quad (12)$$

where $-\Delta H$ is the heat of reaction. This semi-empirical equation can be applied to a heterogeneous atom recombination proceeding by the mechanism



where S is the surface and A the atom; these processes are generally exothermic so that the activation energy is

$$E = 0.055 D_{SA}. \quad (13)$$

D_{SA} is equal to the heat of adsorption $-\Delta H_{ads}$ of the atom on the surface, so that

$$E = -0.055 \Delta H_{ads}; \quad (14)$$

the activation energy for the recombination can therefore be estimated if the heat of adsorption of the atoms is known. It may be noted that this procedure is only applicable to reaction at clean surfaces; if surfaces are contaminated, e.g., with water, the treatment must be modified in the manner to be considered later.

The activation energy can also be estimated from the "desorption temperature," T_d , at which desorption of the atoms becomes appreciable. If Eq. (10), with b_g equal to unity for atomic recombination, is differentiated with respect to T and set equal to zero the result is

$$E/RT_m = 1, \quad (15)$$

where T_m is the temperature at which γ will be a maximum. It has been noted¹⁰ that T_m is approximately equal to T_d , so that Eq. (15) becomes

$$E = RT_d. \quad (16)$$

That these two methods of estimating E give good agreement with experimental values when these are known is shown by the figures in Table I.

THE RECOMBINATION ON DRY OXIDES

Absolute rate constants and recombination coefficients will now be calculated for several types of surfaces. The case of dry oxides will be considered first, as these are the easiest to treat. The oxides may be assumed to resemble glass as far as their surface properties are concerned, and ΔH_{ads} may therefore be taken as -11 kcal (see Table I). It has been found^{3,4} that the number of hydrogen atoms adsorbed per sq. cm of glass is about 1.35×10^{15} , and on the mechanism assumed these adsorbed atoms react directly with gaseous atoms; C_s is therefore taken as $1.35 \times 10^{15} \text{ cm}^{-2}$. Calculation of γ at 300°K on the basis of these values, using Eqs. (10) and (14), gives 5×10^{-2} , in excellent agreement with Smith's values² ranging from 3×10^{-2} to

¹⁰ N. Buben and A. Schechter, Acta physicochimica, U.R.S.S. 10, 371 (1939).

TABLE II. Calculated values of γ and k' for clean glass surfaces.

$T(^{\circ}\text{K})$	γ	$k' \text{ (cm sec.}^{-1}\text{)}$
90	0.46	6.8×10^4
180	0.22	1.1×10^4
200	2.2×10^{-2}	1.1×10^3
300	3.1×10^{-2}	1.9×10^3
400	3.3×10^{-2}	2.4×10^3
550	3.2×10^{-2}	2.8×10^3

6×10^{-2} for the oxides investigated ($\text{ZnO} \cdot \text{Cr}_2\text{O}_3$, Al_2O_3 , K_2CO_3 , K_2SiO_3 , Na_3PO_4).

THE RECOMBINATION ON CLEAN GLASS SURFACES

Hydrogen atoms recombine very rapidly on clean glass surfaces^{11,12} and it is consequently difficult to make accurate quantitative rate measurements. At liquid air temperatures¹¹ the recombination coefficient is close to unity, but at higher temperatures the value becomes smaller.¹³ In the region from -79°C to 99°C the recombination coefficient increases in accordance with an activation energy of about 0.9 kcal.¹⁴ As the temperature approaches the desorption temperature, which is at about 250°C ,³ the coefficient reaches a maximum and then decreases, the order increasing at the same time from unity to two. This effect is due to the depletion of the layer of hydrogen atoms (so that C_s varies with the pressure of hydrogen atoms), and has also been noted for the recombination of methyl radicals on glass¹⁵ and of nitrogen atoms on nickel.¹⁰ The temperature dependence of γ is shown schematically in Fig. 1, the curve being based on the data summarized above.

In the temperature region from -180°C to -80°C the curve can be fitted by Eq. (10) taking $C_s = 1.35 \times 10^{15}$ and $E = 0$; in the region from -80° to 250° it can be fitted with $C_s = 1.35 \times 10^{15}$ and $E = 0.9$ kcal. The calculated recombination coefficients and rate constants so obtained are shown in Table II. These values are of the right order. Roberts¹⁶ states that γ for glass at liquid air temperatures should be somewhat less than unity. The values of γ between 200° and 500°K agree with that found by Smith² for dry oxides and are also in agreement with the observation of Steiner and Wicke¹⁷ that γ on clean glass is several order of magnitudes higher than on water vapor poisoned glass surfaces (see Table IV).

¹¹ K. F. Bonhoeffer, *Zeits. f. physik. Chemie* **113**, 199 (1924).

¹² H. Senftleben and O. Riechmeier, *Physik. Zeits.* **30**, 745 (1929).

¹³ P. Hartek and E. Roeder, *Zeits. f. physik. Chemie* **178**, 396 (1937).

¹⁴ A. L. Robinson and I. Amdur, *J. Am. Chem. Soc.* **55**, 2615 (1933).

¹⁵ F. Paneth and W. Lautsch, *Ber.* **B64**, 2708 (1931); Paneth, Hofeditz, and Wunsch, *J. Chem. Soc.* 372 (1935).

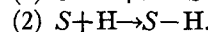
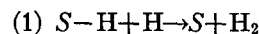
¹⁶ J. K. Roberts, *Some Problems in Adsorption* (The Cambridge University Press, New York, 1939).

¹⁷ W. Steiner and E. Wicke, *Zeits. f. physik. Chemie, Bodenstein Band*, 817 (1931).

TABLE III. Recombination coefficients on water-vapor poisoned glass surfaces.

$T(^{\circ}\text{K})$	Recombination coefficient $\gamma \times 10^5$
93	4.45
193	2.04
288	2.01
453	6.8
573	16.0
723	53.0
863	89.0

In order to explain these results, including the fact that the reaction is of the first order over most of the temperature range, it is proposed that the surface is fully covered by hydrogen atoms, which react with gas-phase hydrogen atoms;



This is consistent with Langmuir's result⁴ that hydrogen atoms are adsorbed on clean glass down to liquid air temperatures, with a packing of about 1.35×10^{15} atoms per cm^2 (the value used by us above); moreover Johnson³ found that desorption only sets in between 200° and 300°C . To explain the fact that the activation energy of the reaction is zero at low temperatures and 0.9 kcal. at higher ones it is suggested that the hydrogen atoms are van der Waals adsorbed to the glass in the low temperature region and chemisorbed at the higher temperatures. Thus R. A. Beebe and his co-workers¹⁸ have shown that in certain cases the heat of adsorption increases with increasing temperature. Support for the mechanism proposed is provided by the fact that, as shown in Table I, the estimated activation energies for the high temperature region are in satisfactory agreement with the experimental values.

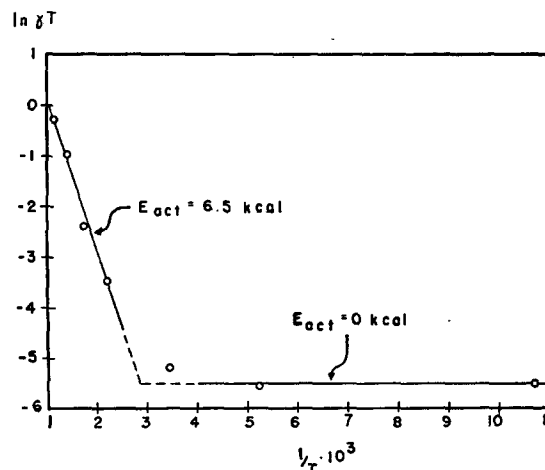


FIG. 2. Plot of $\ln \gamma T$ vs. $1/T$ for the hydrogen atom recombination on glass surfaces poisoned by water vapor.

¹⁸ R. A. Beebe, in G. M. Schwab's *Handbuch der Katalyse* (Verlag Julius Springer, Berlin, 1943), Vol. IV, p. 473 (see e.g., Table 3, p. 494).

TABLE IV. Recombination coefficients and rate constants for atom recombination on H₂O-poisoned glass.

T(°K)	$\gamma(\times 10^6)$		$k'(\text{cm sec.}^{-1})$	
	Calc.	Obs.	Calc.	Obs.
453	5.1	6.8	3.91	(1.96)*
573	18.0	16.0	16.2	
723	47.0	53.0	46.4	
863	81.0	89.0	86.9	

* This value refers to a surface poisoned by syrupy phosphoric acid (I. Amdur, J. Am. Chem. Soc. 60, 2347 (1938)).

THE RECOMBINATION ON WATER VAPOR POISONED GLASS SURFACES

The well-known poisoning effect of water on glass surfaces¹⁹ could be due to two factors, (1) a decrease in the number of active centers, and (2) an increase in activation energy. An increase in activation energy could in turn be due to two causes: (2a) a tighter binding of the adsorbed hydrogen atoms on the poisoned surface as compared with the clean surface, and (2b) the necessity for desorption of the poison in order for the reaction to proceed on the bare surface.

That the poisoning is not due to cause (2b) may readily be shown. The rate of a poisoned first-order reaction occurring only on the bare surface is given by⁸

$$v_1 = \frac{C_g C_s k T F_{gp} f \ddagger}{C_{gp} h F_{gsp}} e^{-(E+E_p)/RT} \quad (17)$$

where E_p is the heat of adsorption of the poison and the subscript gp applies to the poison in the gas phase. The rate is therefore inversely proportional to the partial pressure of the poison in the gas phase, and the same applies to the recombination coefficient; it has, however, been shown by von Wartenberg and Schultze,²⁰ and by Smith,² that the water vapor pressure has no influence on the rate. An additional argument against this explanation stems from the activation energy calculated from Eq. (17) according to the method outlined below. This calculation gives an activation energy $E+E_p$ of 3 kcal. which means that the heat of adsorption of the water vapor on the glass would have to be 3 kcal. or less. In fact, it is much greater in the temperature range where adsorption of H₂O on glass has been observed.

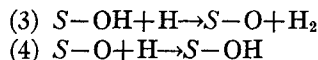
A decision between the two remaining possibilities, i.e., (1) and (2a), can be made by considering the temperature dependence of the rate in more detail. It is evident from Eq. (10) that a plot of $\ln \gamma T$ versus $1/T$ gives the energy of activation, the assumption being that the reaction occurs on a fully covered surface so that C_s is temperature independent; the equations are therefore only applicable up to the desorption temperature. Some values for γ obtained by Smith² are given in Table III, and a plot of $\ln \gamma T$ against $1/T$ is shown in Fig. 2. The activation energy is seen to be zero in the

range from about -180°C to 0°C , and is 6.5 kcal. from 100°C to 600°C ; in the intermediate region from 0°C to 100°C the activation energy varies with the temperature. The high and low temperature mechanisms will now be considered separately.

High Temperature Mechanism

The behavior in the high temperature region can be analyzed more easily, and will therefore be considered first. The value of 6.5 kcal. for the activation energy, as compared with 0.9 kcal. on clean surfaces, indicates that the poisoning is not due to a decrease in the number of reaction sites but to the additional energy required to form hydrogen molecules by reaction between a gas phase hydrogen atom and a hydrogen atom attached to the surface. This is confirmed by the fact that calculated values of γ and k' , employing the activation energy of 6.5 kcal. and 10^{15} for C_s , are in good agreement with the experimental values; the results are shown in Table IV. This value for C_s is the same as that for unpoisoned surfaces. The poisoning is thus shown to be due to cause (2a). The observed value of k' is that of Amdur's²¹ mechanism C, involving first-order wall recombination. Since it has been shown by Smith² and by Poole²² that the recombination coefficient for hydrogen atoms is the same on a phosphoric acid poisoned surface as for one poisoned by water, one can assume the same mechanism in both cases, and it is therefore valid to compare our results with those of Amdur. This mechanism will now be discussed.

It has been shown by van Itterbeck and Vereycken²³ that water in the molecular form is not adsorbed on glass at above 180°C ; the poisoning agent in Smith's experiments must therefore be the hydroxyl radicals formed from the water vapor in the discharge employed by him. The simplest and most plausible recombination mechanism is therefore



where S represents a site on the clean glass surface. The dissociation energy of the free hydroxyl radical is 100 kcal., and the dissociation energy of the first OH bond in water is 118 kcal.;²⁴ the dissociation energy of the OH radical adsorbed on the surface may be expected to fall within that range. On the basis of the lower value reaction (3) is exothermic, and using Hirschfelder's rough procedure the activation energy would be ~ 5.5 kcal.; the upper value on the other hand, would require an endothermic reaction, and Hirschfelder's rule gives $E = \sim 20.7$ kcal. The experimental value of 6.5 kcal. is clearly of the right order to be consistent with the

²¹ I. Amdur, J. Am. Chem. Soc. 60, 2347 (1938).

²² H. G. Poole, Proc. Roy. Soc. A163, 404 (1937).

²³ A. van Itterbeck and W. Vereycken, Zeits. f. physik. Chemie B48, 131 (1941).

²⁴ R. J. Dwyer and O. Oldenburg, J. Chem. Phys. 12, 351 (1944).

¹⁹ R. W. Wood, Proc. Roy. Soc. 97, 455 (1920).

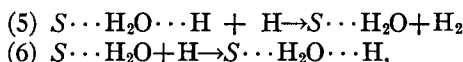
²⁰ H. von Wartenberg and G. R. Schultze, Zeits. f. physik. Chemie B6, 261 (1929).

mechanism, and might be taken to suggest that the OH dissociation energy of the adsorbed radicals is ~ 104 kcal.

Low Temperature Mechanism

The activation energy in the low temperature region has been shown to be close to zero, and this implies that the poisoning mechanism involves a reduction in the number of active sites per sq. cm. Using Eq. (10) it is possible to calculate the value of C_s which will make the calculated values of γ agree with the experimental ones: the result is $1.4 \times 10^{11} \text{ cm}^{-2}$, a reduction by a factor of 10^4 of the value for a normal active surface. This conclusion is in agreement with other results obtained for hydrogen at low temperatures; thus in an analysis of results of J. K. Roberts²⁵ on the adsorption of hydrogen on tungsten between 79°K and 295°K , Laidler, Glass-tone, and Eyring⁸ concluded that the data required C_s to be $\sim 10^{10}$.

At low temperatures water is known to be strongly van der Waals adsorbed on glass, and is probably in the molecular form. The reaction of the gaseous hydrogen atoms cannot be with chemically-bound hydrogen (as the activation energy is zero), but must be with hydrogen atoms van der Waals adsorbed above the water layer. The mechanism proposed can be written as



where the dotted lines indicate van der Waals adsorption. It may be mentioned that van der Waals adsorption of hydrogen atoms on a film of adsorbed water has also been postulated by Roberts²⁵ to explain some of his data.

Note added in proof.—Since the present paper was submitted we have seen a translation of an article by V. V. Voievodsky and G. K. Lavroskaia, *Doklady Akad. Nauk. U.S.S.R.* 63, 151 (1948). (See Chem. Abstracts 43, 1635.) These authors do not discuss any specific recombination or poisoning mechanisms, but their experimental values are consistent with those discussed above.

ACKNOWLEDGMENT

The authors wish to express their thanks to Professors H. M. Hulburt and W. J. Moore for valuable discussions on several points in this paper, and to Dr. W. V. Smith for the loan of a copy of his thesis.

APPENDIX

The Recombination Coefficient for a Flow System

Since the data of Smith² used in this paper were obtained by means of a flow system, it is necessary to show that Eq. (4) for the recombination coefficient in a static system is identical with that derived for a flow system.

In Smith's experiments the hydrogen atoms produced in the discharge tube and pumped through it were allowed to diffuse into a side arm closed on one end and joined perpendicular to the discharge tube on the other. The recombination of the atoms takes place on the walls of this side arm during their diffusion along this side arm.

Let n = number of atoms per cc,
Let x = distance along side arm from discharge tube,
Let D = diffusion coefficient,
Let F = drift velocity of atoms along side arm,
Let γ = coefficient of recombination,
Let V = volume per unit length of side arm,
Let S = surface per unit length of side arm,
Let \bar{v} = mean atomic speed,
Let k = first order rate constant for recombination,
Let r = radius of side arm.

The subscript 0 indicates the junction of the side arm with the discharge tube. It will be assumed that the atomic concentration is constant over the cross section of the side arm so that $n = n(x)$, and $F \neq F(r)$. Smith² has shown that these assumptions are valid under his experimental conditions.

The following equations then hold:

Number of atoms lost to wall per cm per sec.
= gradient of flow through tube

$$(n\bar{v}/4)S\gamma = -V(\partial/\partial x)(nF), \quad (18)$$

and the diffusion equation

$$nF = -D(\partial n/\partial x). \quad (19)$$

Combination of (18) and (19) gives

$$\partial^2 n/\partial x^2 = n\bar{v}S\gamma/4VD. \quad (20)$$

the solution of which is

$$n = A \exp[(\bar{v}S\gamma/4VD)^{1/2}x] + B \exp[-(\bar{v}S\gamma/4VD)^{1/2}x]. \quad (21)$$

For a tube of finite length neither A nor B is equal to zero. The term with the positive exponent, which increases with increasing x , can be considered as representing the stream of atoms reflected from the closed end of the tube, and the term with the negative exponent, which decreases with increasing x , can be considered as representing the incoming stream of atoms from the discharge tube. If the side arm through which the atoms move is long enough so that the atoms will make many collisions with the walls before reaching the end of the tube, most of the atoms will have recombined to molecules, and the stream of atoms reflected from the closed end of the tube will be negligible compared to the incoming stream of atoms. Since the experimental conditions are such that $2r \gg \lambda$, where λ is the mean free path of the atoms, one is in the region of Poiseuille rather than Knudsen flow, and the backward reflection of atoms from the walls of the tube can be neglected. Equation (21) then reduces to

$$n = n_0 \exp[-(\bar{v}S\gamma/4VD)^{1/2}x] \quad (22)$$

under the boundary conditions $n = n_0$ when $x = 0$. Therefore n is expressible as

$$n = n_0 e^{-\beta x} \quad (23)$$

where $\beta = (\bar{v}S\gamma/4VD)^{1/2}$. Substituting (23) into (19) one obtains

$$F = D\beta. \quad (24)$$

It will be noted that not only is $F \neq F(r)$, but also $F \neq F(x)$. The first-order rate constant k is given by the relation

$$n = n_0 e^{-kt}. \quad (25)$$

Replacing the time t by its equivalent $t = x/F$ and expressing F by Eq. (24) gives

$$n = n_0 e^{-kx/D\beta}. \quad (26)$$

Combination of (26) and (23) gives

$$\beta^2 = k/D. \quad (27)$$

Introducing the explicit expression for β and solving for γ ,

$$\gamma = 4kV/\bar{v}S. \quad (28)$$

Since $V = \pi r^2$ and $S = 2\pi r$, Eq. (28) reduces to

$$\gamma = 2kr/\bar{v}, \quad (29)$$

which is identical with Eq. (4) derived earlier.

²⁵ J. K. Roberts, *Proc. Roy. Soc. A* 152, 445 (1935).