meter on a stone-topped table or upon one which has at some time been bespattered with reagents, careful insulation of all batteries from each other and from the table will be necessary. All wiring should be done so that conductors do not touch one another even though they carry "insulation." The cell E to be measured should be placed upon a dry hardwood board, hard rubber or other insulating material. Due to the high amplification obtained, the valves should be kept as free as possible from mechanical vibration. The inner grid of the tetrode should be connected with flexible wire. In some instances connecting the negative side of the filaments to earth may be helpful although in all work done by the writer this has been found unnecessary.

Summary

A device has been described which employs a tetrode and a triode in a simple potentiometer circuit and arranged in such a manner that calibration of the valves and the constancy of their characteristics are unnecessary. Since the apparatus is essentially electrostatic in operation, it is particularly adapted to the measurement of cells having high internal resistance. As only one adjustment is necessary, measurements may be made with comparative rapidity.

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THE SYNTHESIS OF WATER WITH A SILVER CATALYST. II. ENERGY OF ACTIVATION AND MECHANISM

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Introduction

In a number of examples of homogeneous, bimolecular gas reactions it has been shown[1] that the absolute rate of reaction may be expressed by the equation

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = Ze^{-\frac{E}{RT}}$$

where C is the concentration of the reacting species at time t, Z is the number of collisions in unit time per unit of volume, and E is the energy of activation per two moles of reactant. $e^{-E/RT}$ is, therefore, the fraction of the total number of collisions which is effective. Since the fraction of the molecules which have energy of any particular kind, kinetic, rotational, vibrational or electronic, in excess of E calories per mole is also approxi-

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[1] Lewis, *J. Chem. Soc.*, **113**, 471 (1918); Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, **1926**, pp. 50 *et seq.*

mately equal to $e^{-E/RT}$, it has been concluded that all collisions are effective in which at least $E/6.06 \times 10^{23}$ cal. of energy of an appropriate kind are available in the two colliding molecules.

The corresponding hypothesis suggests itself for the rate of reaction between two gases in contact with a solid catalyst, particularly for those cases in which only one of the reactants is adsorbed. It has not been possible to test such an assumption hitherto because catalytic studies have seldom been accompanied by the necessary adsorption measurements, and in the few cases in which these have been carried out it has usually been found that both reactants are adsorbed.[2] While it is conceivable that the hypothesis might be applicable to cases of the latter kind, adequate data are not available on the general problem of adsorption in mixtures.

In a previous paper[3] it was shown that the combination of hydrogen and oxygen in contact with metallic silver is a convenient example for experimental test, since under the conditions employed silver strongly adsorbs oxygen but does not take up hydrogen in measurable quantity. The rate of reaction was found to be proportional to the pressure of hydrogen, independent of the oxygen pressure and markedly retarded by water vapor. Since the oxygen adsorption is nearly independent of the pressure, these results are evidently in qualitative agreement with the hypothesis that the reaction mechanism depends on collisions of gaseous hydrogen molecules with those parts of the surface which are covered by adsorbed oxygen but free from adsorbed water. Since the previous work did not include measurements of the adsorption of water vapor, it was not possible to test the hypothesis quantitatively.

The necessary adsorption measurements have now been carried out on a new silver catalyst and the reaction kinetics have been redetermined for this new sample at two temperatures. The results are found to be in agreement with the hypothesis that reaction occurs at every collision of hydrogen with "dry" adsorbed oxygen in which the total energy available on collision exceeds the true energy of activation.

Apparatus and Procedure in Kinetic Experiments

The apparatus and procedure were the same as those employed previously,[3] with one exception. It was feared that when the hydrogen–oxygen mixtures entered the catalyst dry, as in the earlier work, the greater freedom from adsorbed water at the entering end of the catalyst would lead to so great an evolution of heat due to reaction at this point

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[2] See, for example, the extensive studies by Pease and collaborators on the combination of ethylene and hydrogen in contact with various metals, THIS JOURNAL, **45**, 1196, 2235, 2296 (1923); **47**, 1235 (1925); **49**, 2503, 2783 (1927).

[3] Benton and Elgin, THIS JOURNAL, **48**, 3027 (1926).

that even the high thermal conductivity of silver might be insufficient to prevent a considerable temperature gradient in the catalyst. For this reason the present experiments were carried out with a constant concentration of water vapor in the entering gases, amounting to approximately 10% by volume.

The introduction of this water vapor was accomplished by adding the desired quantity of hydrogen to the oxygen stream, or *vice versa*, and passing the mixture over heated platinized asbestos or copper oxide.[4] The mixture of oxygen and water vapor thus produced, after uniting with a current of hydrogen in the desired proportion, was passed downward over the silver catalyst. All tubing through which water vapor passed was heated externally by passing an electric current through coils of chromel wire in order to avoid condensation. The total rate of flow of the gas mixture entering the catalyst was in all cases 50 cc. per min. (0°, 760 mm.).

The silver catalyst was obtained from another sample of the silver oxide previously employed and the reduction with hydrogen at low temperature was carried out in the manner already described, the final temperature being 100°. Preliminary experiments with the catalyst thus prepared showed that the activity was inconveniently high, since hydrogen-oxygen mixtures were exploded when passed over it at room temperature. It was therefore heated in hydrogen at 310° for four hours to reduce its activity to a suitable value. The mass was cylindrical in shape, 3 cm. in diameter and approximately 5 cm. high, giving an apparent volume of 35 cc. The weight was 47.70 g.

The method of procedure was the same as previously reported. To avoid possible uncertainties due to previous history, the catalyst was given a uniform treatment before every experiment, consisting in heating in hydrogen at 96° for one hour. Check runs were made alternately throughout the investigation. Correction for the small changes in activity which were thus observed was made by adding to, or subtracting from, the yield in each run the percentage amount per run necessary to bring the checks into agreement.

Results of Kinetic Experiments

The results of the experiments on reaction kinetics are given in Table I in the order in which they were made. The values for the observed yields, in the next to the last column, represent the net water formation after subtracting the 20.2 mg. per five minutes present in the entering gas.

The values in Cols. 5 and 6 were calculated as follows. The pressure of hydrogen in the entering gas is V_HP/V, where V_H and V are the volumes (at 0°, 760 mm.) of hydrogen and total gas, respectively, entering the catalyst per five minutes and P is the corrected barometric pressure.[5] The hydrogen pressure in the exit gas is

$$\frac{V_H - \frac{22.4}{18}Y}{V - \frac{11.2}{18}Y}P$$

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[4] Copper oxide was found preferable to platinized asbestos, as the use of the latter occasionally led to mild explosions.

[5] The pressure drop in the catalyst bed was negligible at a rate of flow of 50 cc. per min.

TABLE I

REACTION KINETICS

Total flow, 50.0 cc. per min. (0°, 760 mm.). Water in entering gas 20.2 mg. per 5 min. Excess oxygen.

Run	Temp., °C.	Ent. H, cc. per min.	Barometer, mm. at 0°	Av. H press., mm.	Av. water press., mm.	Yield, mg. of water per 5 min.		
						Calcd.	Obs.	Corr. for activity
10	94	10.04	744.9	139.1	88.1	40.4	6.2	7.8
11	108	10.04	749.1	123.7	105.6	40.4	15.2	18.3
12	94	10.04	747.2	138.5	88.7	40.4	6.8	7.8
13	108	2.51	750.0	29.0	84.0	10.1	4.7	5.1
14	94	10.04	748.8	137.6	90.3	40.4	7.5	7.8
15	108	5.02	748.5	59.2	92.1	20.2	8.8	9.0
16	94	10.04	750.0	137.3	91.0	40.4	7.8	7.8
17	108	17.57	749.1	219.0	131.1	70.7	26.8	26.9
18	94	10.04	747.6	137.0	90.5	40.4	7.7	7.8
19	108	25.10	746.0	321.0	148.5	101.0	34.7	34.9
20	94	10.04	744.2	136.1	90.3	40.4	7.8	7.8
21	94	2.51	741.0	32.1	78.5	10.1	2.6	2.6
22	94	10.04	742.3	135.8	90.1	40.4	7.8	7.8
23	94	5.02	745.1	66.8	83.5	20.2	4.6	4.9
24	94	10.04	746.6	138.2	88.8	40.4	6.9	7.8
25	94	17.57	747.6	245.7	95.7	70.7	10.7	12.7
26	94	10.04	748.5	139.6	87.8	40.4	6.3	7.8
27	94	25.10	750.3	354.5	105.0	101.0	14.8	17.6
28	94	10.04	748.5	138.7	88.8	40.4	6.8	7.8

where Y is the observed yield in mg. of water per five minutes. Hence the average hydrogen pressure is

$$P_H = \frac{P}{2}\left(\frac{V_H}{V} + \frac{V_H - \frac{22.4}{18}Y}{V - \frac{11.2}{18}Y}\right)$$

Similarly, the average pressure of water vapor (P_W) has been calculated from the expression

$$P_W = \frac{22.4}{18}\cdot\frac{P}{2}\left(\frac{20.2}{V} + \frac{20.2 + Y}{V - \frac{11.2\,Y}{18}}\right)$$

An attempt was made (Runs 5 and 9) to use mixtures containing an excess of hydrogen, but such experiments were always followed by a permanent decrease in catalytic activity. This effect is probably attributable to the fact that at the higher rates of reaction obtained with excess hydrogen, the catalyst surface is kept comparatively free from adsorbed oxygen with the result that local overheating causes a sintering of the active surface.

An earlier series of kinetic experiments was carried out with another catalyst, using 10 mg. of water per five minutes in the entering gas. The results are omitted because an explosion destroyed the catalyst before its adsorptive power had been determined. The general character of the results is similar to those in Table I, and the data are fitted by the same type of kinetic equation.

Apparatus and Procedure in Adsorption Experiments

The amount of oxygen adsorbed by the catalyst was determined by the static method described in the previous paper.

The adsorption of water was determined by a flow method. Mixtures of water vapor with oxygen or hydrogen in proper proportions to give the desired partial pressure were passed over the catalyst, heated in a suitable vapor bath, until equilibrium was reached. The water in the entering gas was then shut off and the water adsorbed plus that in the free space was swept out and collected in a calcium chloride weighing tube. At the conclusion of these measurements the catalyst bulb was removed from the kinetic apparatus and sealed to the apparatus used for the determination of the oxygen adsorption. After removal of the adsorbed oxygen by treatment with hydrogen the free space in the bulb and connecting capillary was determined with hydrogen, which had previously been shown not to be measurably adsorbed by a silver catalyst. From this measured volume the weight of water in the free space at any partial pressure could be calculated, and hence the amount adsorbed.

Results of Adsorption Experiments

When mixtures of water vapor with hydrogen are used the adsorption of water occurs on a bare silver surface, since hydrogen is not adsorbed at the temperatures in question. Under the conditions of the catalysis, however, it has been shown that the surface is largely covered with adsorbed oxygen, and it is the adsorption of water by such a surface that is

TABLE II

ADSORPTION OF WATER VAPOR BY THE CATALYST

Partial press., mm. of Hg	Total water found Mg.	Total water found Cc.	Water in free space, cc.	Water adsorbed, cc.
Series 1.	Temperature 110°.		Oxygen covered surface	
75	9.4	11.7	3.7	8.0
175	15.0	18.6	8.5	10.1
275	19.6	24.3	13.3	11.0
75	8.8	10.9	3.2	7.7
Series 2.	Temperature 100°.		Oxygen covered surface	
75	9.4	11.7	3.3	8.4
175	15.2	18.8	7.8	11.0
275	19.4	24.1	12.2	11.9
Series 3.	Temperature 100°.		Bare surface	
75	3.8	4.7	3.3	1.4
175	9.4	11.7	7.8	3.9
275	14.0	17.4	12.2	5.2

of importance in the reaction kinetics. For this reason the majority of the measurements were made with mixtures of oxygen and water vapor (Series 1 and 2, Table II). Three partial pressures of the latter gas were used, covering the range obtaining in the kinetic experiments, at each of two temperatures, 100° (boiling water) and 110° (boiling toluene). The results are shown in Table II. The volumes given are those at 0° and 760 mm. After the first three measurements in Series 1, the catalyst was transferred to a new bulb of somewhat smaller volume than the original.

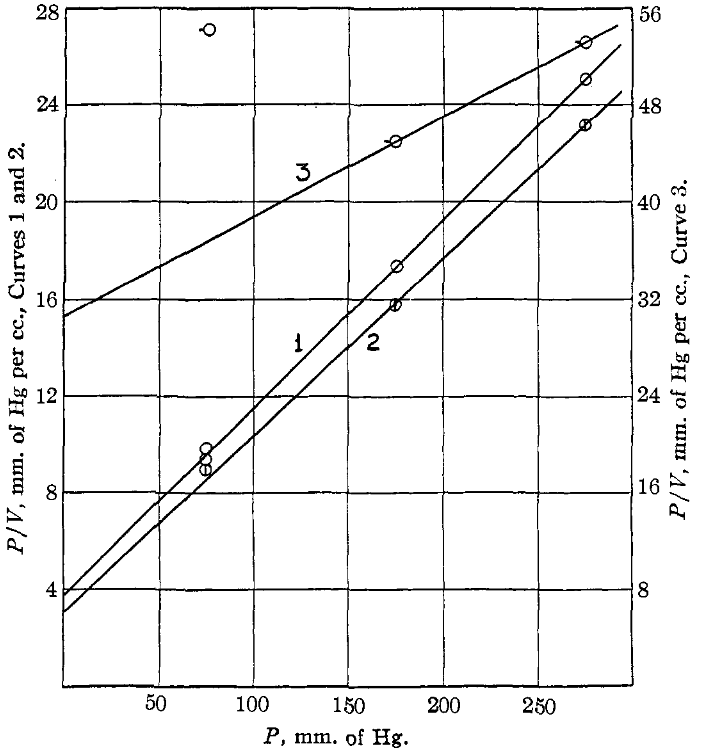

Fig. 1.—Adsorption of water vapor by the catalyst. Curves 1 and 2: oxygen-covered surface at 110 and 100°, respectively. Curve 3: bare surface at 100°.

These results are not even approximately fitted by an isotherm of the Freundlich type but agree well with the simplest form of adsorption equation derived by Langmuir[6] on the hypothesis of a unimolecular layer, namely $V = V_0aP/(1 + aP)$, where V and V_0 are the volumes adsorbed at pressure P and at infinite pressure, respectively, and a is a constant at a given temperature. This may be put in the form $P/V = 1/aV_0 + P/V_0$. A plot of P/V against P should, therefore, yield a straight line

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[6] Langmuir, This Journal, **40**, 1370 (1918).

whose slope and intercept permit a calculation of a and V_0. The results of the three series of measurements have been plotted thus in Fig. 1. With the exception of the lowest point in Series 3, where the experimental error may be relatively great, the straight lines drawn in the figure fit the data closely. For Series 1, 2 and 3, respectively, the values of the constants are: V_0 = 12.8, 13.7, 12.1; a = 0.0209, 0.0236, 0.0027.

It may be noted that although the bare surface adsorbs much less water at a given pressure than the oxygen-covered surface, the maximum adsorptions at saturation (V_0) are nearly the same. However, the adsorption of oxygen by this catalyst at 110° was found to be 6.2 cc. (0°, 760 mm.), a value which is approximately half that obtained for water vapor.

The simplest interpretation of these facts seems to be as follows. Since the results of the previous work show that the adsorption of oxygen by silver catalyst is nearly independent of pressure and temperature over the range in question, it appears probable that this gas is taken up in a monatomic layer such that each silver atom in the surface is covered by one adsorbed oxygen *atom*. In the absence of oxygen, each exposed silver atom may take up one molecule of water, so that the volume of the latter gas adsorbed at saturation is twice as great as for oxygen molecules. When the surface is covered with oxygen, each atom of the latter can hold one molecule of water. Since the oxygen adsorption is irreversible, there can be no question of a displacement of the adsorbed oxygen by water vapor, and we conclude, therefore, that the water is held in a second layer on top of the oxygen layer.

Although in the light of previous work on adsorption by metallic catalysts the above assumption that the oxygen is taken up in a monatomic layer appears most probable, nevertheless it is obvious that other assumptions are possible, for example, that each silver atom is covered by one oxygen *molecule*, or perhaps that two silver atoms are required to saturate each oxygen atom. In either case the conclusions to be drawn in regard to the mechanism of the reaction between hydrogen and oxygen will not be seriously affected. This will be clear from the facts, first, that these alternative assumptions do not affect the calculations of the next paragraph on the retarding action of water vapor, because these calculations do not require a knowledge of the absolute surface of the catalyst, but only of the fraction covered by water; and, second, that the doubling or halving of the calculated absolute surface which these assumptions would require would alter the value of the energy of activation as found below by about 500 cal., which is less than the possible experimental error.

Calculation of Fraction of Surface Free from Adsorbed Water

Taking the above interpretation as substantially correct, and assuming that at the temperatures employed hydrogen is incapable of reacting with those adsorbed oxygen atoms which are covered with adsorbed water, we can calculate the retarding influence of water vapor on the reaction. If we denote by Θ the fraction of the adsorbed oxygen atoms which are covered by water under any given conditions, then $\Theta = V/V_0 = aP/(1 + aP)$. The fraction not so covered is $1 - \Theta = 1/(1 + aP)$.

If the values of a obtained in the previous section are inserted in this equation, approximate values of $1 - \Theta$ may be obtained, but it has seemed best to proceed in a somewhat different manner. From the values of V_0 already given, it is evident that the limiting adsorptive capacity for water is appreciably greater at 100° than at 110°. This probably means that as we approach a point at which the vapor is saturated, some of the adsorbed oxygen atoms become capable of taking up a second molecule of water. To overcome this difficulty, we may calculate the values of a as follows. Noting that when $\Theta = 1/2$, $a = 1/P$, and assuming as before that the total surface is measured by the 6.2 cc. of oxygen adsorbed, we may take the value of a at each temperature as the reciprocal of the pressure at which 6.2 cc. of water vapor are adsorbed. From Series 1 and 2 of Fig. 1, these values are found to be 0.0224 mm.$^{-1}$ at 110° and 0.0284 mm.$^{-1}$ at 100°.

From the derivation of the adsorption isotherm as given by Langmuir,[6] it may be shown that the variation of a with temperature should follow an equation of the form

$$\frac{\mathrm{d}\log a/T^{1/2}}{\mathrm{d}(1/T)} = \frac{Q}{4.58} = \text{constant} \qquad (1)$$

Accordingly, $\log a/T^{1/2}$ was plotted against $1/T$, and a straight line drawn through the two observed points. In this way values of a were obtained for the temperatures used in the catalysis: 0.0233 at 108° and 0.0327 at 94°.

Calculation of Specific Reaction Rate Constant

In the earlier paper it was shown that the kinetics of this reaction in flow system follow the equation

$$Y = \frac{k\cdot P_{\mathrm{H}}}{1 + aP_{\mathrm{W}}} \qquad (2)$$

where Y is the rate of reaction in mg. of water per five minutes, P_{H} and P_{W} are the averages of the entering and exit pressures (in mm. of mercury) of hydrogen, and water vapor, respectively, and k is the specific reaction rate constant. Considerations outlined in another place[7] show that when, as in these experiments, the conversion does not exceed 50% no serious error is introduced by the use of these arithmetical average pressures instead of the true averages obtained by integration.

From the values of a obtained in the previous section and from the data

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[7] Benton, *Ind. Eng. Chem.*, **19**, 494 (1927).

of Table I, the values of k in Equation 2 may now be calculated. The results are given in Table III.

Table III

Specific Reaction Rate Constants

Temperature, 108°			Temperature, 94°		
Run	$1 + aP_W$	k	Run	$1 + aP_W$	k
13	2.96	0.521	21	3.56	0.293
15	3.14	.477	23	3.73	.274
11	3.46	.513	24	3.90	.220
17	4.06	.498	25	4.13	.214
19	4.46	.485	27	4.44	.220
	Av.,	.499		Av.,	.244
				Av. of last 3,	.218

Some inconsistency is evident in the results at 94°, particularly in Runs 21 and 23, where the smallness of the observed yields involves a relatively large experimental error. For this reason the average of the last three runs at 94° is considered more reliable than the average of all five runs. With the exceptions noted, Equation 2 is satisfactorily confirmed.

Calculation of True Energy of Activation

According to Arrhenius' original formulation[8] of the effect of temperature on reaction rate, the energy of activation, E, may be calculated from the equation $k \propto e^{-E/RT}$, where R is the gas constant per mole and T is the absolute temperature. For reactions in which the rate is proportional to the collision frequency, however, a slight modification is necessary,[9] since the rate of collision is itself a function of temperature. At constant pressure the rate at which gas molecules collide with a solid surface is inversely proportional to the square root of the absolute temperature; accordingly, the variation of k with temperature should follow the equation $k \propto T^{-1/2}\, e^{-E/RT}$. Taking logarithms on both sides, and solving for E, we obtain

$$E = \frac{4.58 T_1 T_2}{T_1 - T_2} \log \frac{k_1\, T_2^{1/2}}{k_2\, T_1^{1/2}}$$

From the averages given in Table II ($T_1 = 381$, $k_1 = 0.499$, $T_2 = 367$, $k_2 = 0.218$), E is found to be 16,800 cal. per mole of water formed. If k_2 is taken as 0.244, $E = 14{,}600$. The unmodified Arrhenius equation leads to values about 250 cal. smaller.

Since measurements of water adsorption were not made on the catalyst employed in the earlier work, the true energy of activation can be calculated from the data there obtained only on the assumption that the same values of the adsorption constant, a, are applicable to both catalysts.

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[8] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[9] Compare Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, **1926**, p. 100.

This assumption is not altogether unreasonable, since it does not require that equal quantities of water be adsorbed by the two catalysts, but only that the shape of the adsorption isotherms be similar at equal temperatures. On this assumption we have calculated from Equation 1 values of a for the original catalyst at the temperatures used, and have employed these to determine the reaction rate constants, k, and the energy of activation. From the data of Tables I and VI of the earlier paper, E is found in this way to be 15,900 (Table I), 16,100 (Table VI, First Series) and 15,600 (Table VI, Second Series).[10]

From a consideration of these several calculations, we may take the value of the energy of activation obtained from the temperature coefficient as 16,000 cal., with an uncertainty of perhaps 1000 cal.

Test of Collision Mechanism of Reaction

On the basis of the proposed mechanism, every collision of gaseous hydrogen with adsorbed oxygen, which is free from adsorbed water, should be effective, in which the total energy available in the collision exceeds the energy of activation, E. In the previous paper it was shown that the rate of collision (R) of hydrogen with the surface, expressed in terms of the equivalent milligrams of water per five minutes, is

$$R = \frac{2.22 \times 10^5}{\sqrt{T}} \cdot S \cdot P_H$$

where S is the area, in sq. cm., of the surface occupied by adsorbed oxygen. If we denote by f the fraction of these collisions which are effective, it is evident that the specific reaction rate constant, k, is given by the equation

$$k = \frac{2.22 \times 10^5}{\sqrt{T}} \cdot S f \qquad (3)$$

If the energy of activation is furnished entirely by the impinging hydrogen or entirely by the adsorbed oxygen, or however it may be distributed between the two, the fraction of the collisions in which the total energy available is in excess of E is given approximately by the expression $e^{-E/RT}$.

The surface area S which is occupied by oxygen may readily be calculated on the assumption that the adsorption of this gas represents a monatomic layer in which a single oxygen atom is attached to each adsorbing silver atom. The argument in favor of this assumption has been given in a previous section. On this basis, the 6.2 cc. (0°, 760 mm.) of oxygen adsorbed by the catalyst represents a surface containing 3.4×10^{20} silver

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[10] In the earlier paper it was stated incorrectly that the observed energy of activation would necessarily be *reduced* when corrected for the change of water adsorption with the temperature. This statement overlooked the fact that the higher partial pressure of water vapor corresponding to the increased yields at the higher temperature may more than counterbalance the decrease in the constant a.

atoms. Since the molecular volume of silver is 10.3 cc., each silver atom occupies 1.70×10^{-23} cc., and the area assignable to each atom in the surface is $(1.70 \times 10^{-23})^{2/3}$, or 6.6×10^{-16} sq. cm. Hence the adsorbing surface of the catalyst is 2.2×10^5 sq. cm.

Inserting this value of S in Equation 3, we obtain

$$k = \frac{4.9 \times 10^{10}}{\sqrt{T}} e^{-\frac{E}{RT}}$$

From this equation, with E taken as 16,000 cal., the calculated values of k are 1.9 at 108° and 0.88 at 94°, which may be compared with the experimental values of 0.50 and 0.22, respectively. Owing to the exponential form of the equation, however, a better comparison may be obtained by inserting the observed values of k, and calculating E. In this way E is found to be 16,900 cal. The discrepancy between the two values of E is probably within the possible limit of experimental error.

It may be mentioned that the value of the surface area employed in this calculation is certainly too large. Measurements reported in the previous paper showed that while at least half of the oxygen adsorption occurs practically instantaneously, the remainder of the gas is taken up with great slowness, so that the quantity of oxygen actually on the surface during a catalytic experiment must be less than the amount present when adsorption equilibrium has been established. From a consideration of the relative rates at which oxygen is adsorbed and removed by reaction with hydrogen it appears that the quantity actually present on the surface during the catalysis was only about half as great as the value found in the adsorption measurements. When the new value of S thus obtained is employed in Equation 3, the value of E calculated from either of the observed values of k is 16,400 cal.

Conclusion

Although the results confirm the hypothesis that reaction occurs at every collision of hydrogen with "dry" adsorbed oxygen, in which the energy available on collision exceeds the energy of activation, no information is furnished as to the proportion in which this energy is contributed by each of the reacting species, or the kinds of energy involved. If the hydrogen must be in an exceptional energy state, this energy is presumably either kinetic or rotational or both, since the specific heat at the temperatures in question shows the absence of vibrational energy, and electronic excitation is precluded by the small magnitude of the energy of activation observed.

The theory of the catalytic surface proposed by Taylor[11] postulates that the surface of a typical catalyst is composed of atoms of widely

[11] Taylor, *Proc. Roy. Soc., London,* **108A,** 105 (1925).

varying catalytic activity. If this view is correct in the case of silver, it would follow that collisions of hydrogen with oxygen adsorbed on the most active parts of the surface would be much more effective than elsewhere. Thus the energy of activation calculated from the observed reaction rates would represent a statistical average taken over the whole surface, varying from very small energies of activation for the most active spots to very high energies for the least active spots. The energy of activation calculated from the temperature coefficient of the reaction rate would represent a similar average, since the activity of the relatively inactive spots must increase more rapidly with temperature than the activity of those which are already more active. Hence it would appear that, while the results of this investigation do not lend any additional support to the theory of active spots, they can probably be satisfactorily reconciled with it.

Summary

An earlier study of the rate of combination of hydrogen and oxygen in contact with a silver catalyst has been in part repeated and extended to include measurements of the adsorption of all the gases concerned. The principal results are as follows.

1. Hydrogen is not measurably adsorbed by the catalyst under the conditions employed but oxygen is strongly adsorbed and to an extent nearly independent of temperature and pressure. The effective surface area of the catalyst has been calculated from the oxygen adsorption, on the assumption that the latter represents a monatomic layer.

2. Water vapor is somewhat adsorbed by a bare silver surface but much more strongly when the surface is already occupied by adsorbed oxygen. The results follow adsorption isotherms of the Langmuir type and permit a calculation of the fraction of the surface free from adsorbed water under the conditions of the catalysis.

3. The rate of the reaction is found to be independent of the pressure of the oxygen but proportional to the hydrogen pressure and to the fraction of the surface free from adsorbed water. The true energy of activation, obtained from the temperature coefficient, is 16,000 cal., with an uncertainty of about 1000 cal.

4. It has been found that the absolute rate of reaction agrees with that calculated on the hypothesis that reaction results from every collision of gaseous hydrogen with "dry" adsorbed oxygen in which the total energy available on collision exceeds 16,400 cal. Since these two values of the energy of activation differ by less than the experimental error, the hypothesis is considered to be confirmed for this particular reaction.

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