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# The Activated Adsorption of Hydrogen on Chromic Oxide Gel. The Effect of Gas Pressure[1]

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The work of Pace and Taylor[2] and that of Kohlschütter[3] established that the rate of activated adsorption of hydrogen was the same as that of deuterium on zinc chromite, nickel and chromic oxide at a pressure of one atmosphere and within limited temperature ranges. These results seemed incompatible with certain earlier theories of the mechanism of activated adsorption. One of the theories had been that every molecule was adsorbed which struck a suitable section of the surface of the adsorbent with an energy in excess of the calculated activation energy. On the basis of this mechanism, one might expect the different zero-point energies of hydrogen and deuterium to lead to different rates of adsorption. But even if the zero-point energy effects were to cancel, one would still predict that a difference in rate would arise from the difference in the translational velocities of the two gases. Since the ratio of the velocities of hydrogen and deuterium molecules is $\sqrt{2}$, the ratio of the numbers of hydrogen and deuterium molecules striking a unit area in unit time at the same temperature and pressure is also $\sqrt{2}$.

It was felt that an investigation of the effect of pressure upon activated adsorption would lead to results which might materially assist in clarifying the mechanism of this reaction. In such a study one could vary the rate at which molecules strike the surface without the possibility of simultaneously introducing effects resulting from zero-point energy differences.

For this purpose an investigation of the rate of adsorption of hydrogen on chromic oxide gel appeared most suitable by reason of its characteristics already exhibited in the work of Howard[4] and Kohlschütter.[3]

## Experimental

The apparatus was designed to measure the velocity of adsorption at constant pressure and was that of Strother[5] with a modification of the manometer system. In Strother's apparatus the compensating manometer system was always sealed off at one atmosphere pressure. Pressures lower than one atmosphere were obtained by adjusting the mercury level on the compensating system side of the control manometer at a point proportionately below the tungsten contact on the adsorption system side. To avoid the fluctuations in density of this unbalanced mercury column with the fluctuations in the temperature of the room, in the present arrangement, the zero of the compensating system was at the level of the tungsten contact and the pressure inside the compensating system could be varied. The pressure in this latter system could be determined by another manometer. Two identical systems were used and runs could be made concurrently.

The catalyst was evacuated with an oil pump and a mercury vapor pump in series. During evacuation the catalyst was heated with an electric furnace, the temperature of which was determined by a thermocouple. Since

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(1) This paper is an abstract of a thesis submitted by Mr. R. L. Burwell, Jr., to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. A copy of the complete thesis may be borrowed from the Princeton University Library through Inter-Library Loan.

(2) Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

(3) Kohlschütter, *Z. physik. Chem.*, **A170**, 300 (1934).

(4) H. S. Taylor and J. Howard, THIS JOURNAL, **56**, 2259 (1934).

(5) H. S. Taylor and C. O. Strother, *ibid.*, **56**, 586 (1934).

TABLE I

HYDROGEN ADSORPTION ON 15 G. OF PREPARATION NO. 9 AT 1 ATM. PRESSURE AND VARIOUS TEMPERATURES

| Time, min. | Temperature of run, °K. 195 | 273 | 329 | 353 | 383.5 | 405 | 427 | 457 | 491 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | 4.475 | 2.45 | | 1.55 | 1.65 | 1.65 | 2.25 | 4.5 |
| 2 | 17.55 | 4.6 | 2.575 | 1.9 | 1.725 | 1.875 | 1.95 | 3.15 | 6.85 |
| 4 | 17.70 | 4.775 | 2.675 | 2.075 | 1.925 | 2.2 | 2.45 | 4.65 | 10.7 |
| 8 | | 4.95 | 2.8 | 2.225 | 2.225 | 2.6 | 3.3 | 6.95 | 16.3 |
| 20 | | 5.2 | 3.025 | 2.525 | 2.725 | 3.45 | 5.0 | 12.05 | 27.5 |
| 40 | 18.0 | 5.35 | 3.2 | 2.85 | 3.25 | 4.45 | 7.25 | 17.8 | 38.6 |
| 60 | 18.1 | 5.475 | 3.325 | 3.025 | 3.6 | 5.25 | 9.0 | 22.05 | 44.75 |
| 100 | 18.20 | 5.575 | 3.475 | 3.325 | 4.25 | 6.6 | 11.95 | 28.6 | 50.6 |
| 140 | 18.25 | 5.65 | | 3.575 | 4.725 | 7.675 | 14.35 | 33.6 | 53.05 |
| 180 | 18.30 | 5.725 | | 3.775 | 5.175 | 8.625 | 16.45 | 37.55 | |

it was unsafe to heat the catalyst above 400° because of the danger of causing it to undergo the "glow" phenomenon, impractically long times would have been required completely to free the catalyst from adsorbed hydrogen. It was found that seven hours of evacuation at 387 ± 4° brought the catalyst surface to a reasonably reproducible condition.

**Gases.**—Hydrogen and helium were obtained and purified as described by Strother.[5]

**Chromic Oxide.**—Adsorption measurements were made on Preparations 6, 9 and 10 prepared by addition of 0.1 *N* ammonia solution to an electrically stirred 0.1 *N* solution of chromic nitrate. With Preparation 6, the ammonia was added very slowly until the solution was just basic to methyl red, somewhat less than the theoretical amount. The gel settled badly, was washed but once by decantation, filtered, dried in air and then at 110 and 250° successively. With Preparations 9 and 10, the slow addition of a stoichiometrical quantity of ammonia was interrupted for four hours at the mid-point but stirring continued. In No. 9 the final half of the ammonia was added slowly and in No. 10 rapidly in each case with stirring. These precipitates settled well, were readily washed by decantation and dried in three stages at 45, 110 and 250°. The weights of catalyst employed after this treatment were: No. 6, 16.5 g.; No. 9, 15.0 g.; No. 10, 16.0 g.

Two gels, Nos. 7 and 8, prepared by reaction of chromic nitrate and urea in solution at 100° for two and one-half hours, settled readily were easily washed and dried, but on reducing in hydrogen below 400° underwent the glow phenomenon and had small absorption capacity, 1.5 cc. per 24 g. at 527°K. in one hour.

The experimental results were obtained on samples which were, after preparation, reduced in hydrogen at temperatures rising to 390°. Evacuation by a mercury vapor-oil pump series was standardized at 387 ± 4° for seven hours. We know that gels so prepared still contain much water but give reasonably reproducible rates of adsorption.

TABLE II

RUNS ON PREPARATION 9 AT 1/2 ATM. PRESSURE

| Time, min. | Temperature of run, °K. 383.5 | 405 | 427 | 457 | 491 |
|---|---|---|---|---|---|
| 1 | 0.92 | 1.00 | 1.05 | 1.40 | 3.15 |
| 2 | 1.04 | 1.15 | 1.30 | 2.00 | 4.95 |
| 4 | 1.18 | 1.325 | 1.65 | 3.00 | 7.85 |
| 8 | 1.34 | 1.625 | 2.20 | 4.70 | 12.25 |
| 20 | 1.68 | 2.225 | 3.45 | 8.30 | 21.25 |
| 40 | 2.05 | 2.95 | 5.00 | 12.60 | 30.85 |
| 60 | 2.31 | 3.525 | 6.30 | 16.05 | 37.15 |
| 100 | 2.74 | 4.475 | 8.45 | 21.30 | |
| 140 | | 5.325 | 10.30 | 25.45 | |
| 180 | | 6.05 | 11.90 | 28.95 | |

TABLE III

RUNS ON PREPARATION 9 AT 1/4 ATM. PRESSURE

| Time, min. | Temperature of run, °K. 273 | 383.5 | 405 | 427 | 457 | 491 |
|---|---|---|---|---|---|---|
| 1 | | | 0.575 | 0.60 | 0.90 | 1.90 |
| 2 | 1.825 | 0.70 | .65 | .725 | 1.25 | 3.30 |
| 4 | 1.95 | .80 | .80 | .95 | 1.95 | 5.40 |
| 8 | 2.075 | .925 | .975 | 1.30 | 3.05 | 8.65 |
| 20 | 2.25 | 1.175 | 1.375 | 2.125 | 5.60 | 15.55 |
| 40 | 2.40 | 1.45 | 1.85 | 3.175 | 8.80 | |
| 60 | 2.50 | 1.65 | 2.225 | 4.075 | 11.30 | |
| 100 | 2.60 | 1.975 | 2.85 | 5.60 | 15.40 | |
| 140 | | 2.225 | 3.425 | 6.90 | | |
| 180 | 2.675 | 2.45 | 3.925 | 8.05 | | |

TABLE IV

HYDROGEN ADSORPTION ON 16 G. PREPARATION NO. 10 AT 457°K. AND VARIOUS PRESSURES

| Time, min. | 1 Atm. 353°K. | Pressure, atm. 1 | 0.5 | 0.25 | 0.125 |
|---|---|---|---|---|---|
| 1 | | 2.45 | 1.60 | 0.90 | 0.425 |
| 2 | 1.85 | 3.50 | 2.20 | 1.30 | .70 |
| 4 | 2.025 | 5.15 | 3.35 | 2.05 | 1.15 |
| 8 | 2.175 | 7.70 | 5.15 | 3.25 | 1.925 |
| 20 | 2.475 | 13.10 | 9.05 | 5.95 | 3.725 |
| 40 | 2.75 | 19.20 | 13.70 | 9.35 | 6.075 |
| 60 | 2.925 | 23.75 | 17.30 | 12.05 | 8.00 |
| 100 | 3.175 | 30.45 | 22.85 | 16.35 | |
| 140 | 3.425 | 35.40 | 27.10 | | |
| 180 | 3.60 | | 30.65 | | |

## Experimental Results

We summarize, in the following, data from 30 runs on No. 6, 68 runs on No. 9 and 32 runs on No. 10, within the temperature limits 85 to 491°K. and 0.125 to 1 atm. pressure. Within reasonable limits, the several preparations all exhibit the same phenomena. Tables I to IV present the volumes of hydrogen, corrected to N. T. P., adsorbed at various time intervals for different preparations, at varying temperatures and a single pressure, and at one temperature for different pressures. The bulk of the data refer to Preparation 9, which, at a temperature of 82.9°K., adsorbed the following amounts of gas expressed as cubic centimeters per gram at various pressures: 30 mm., 5.6; 200 mm., 10.4; 760 mm., 17.2.

The maximum deviation from the mean in at least two experiments under any given operating conditions was 4%. The normal deviation was about 2%.

## Discussion of Experimental Results

**Effect of Preparation.**—The adsorption measurements indicate clearly that a slow initial rate of addition of ammonia in the preparation leads to high adsorptive capacity.[3] If after the addition of half the calculated quantity of ammonia, the addition is interrupted for a period of time, slow or rapid addition of the final half of the ammonia does not affect materially the adsorptive capacity of the product.

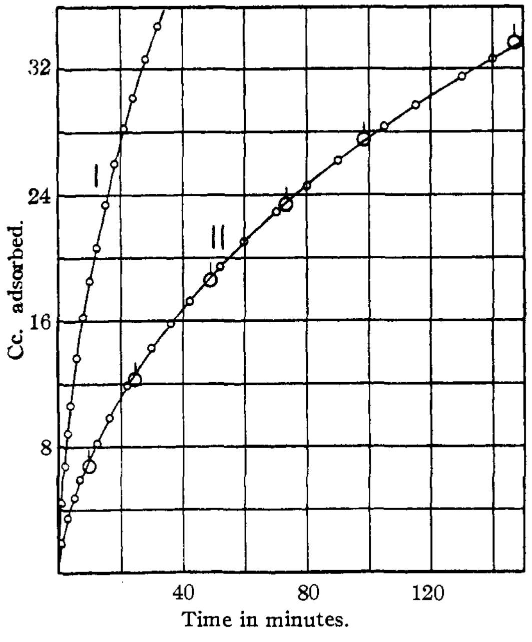

Fig. 1.—Rates of adsorption on preparation 9 at 1 atm.: I, 491°K., av. of runs 18 and 19; II, 457 °K., av. of runs 17 and 23; ó I, with subst., $t' = 4.9\ t$.

**Effect of Temperature.**—In Fig. 1 are plotted the time–adsorption curves for 457 and 491°K. at pressures of one atmosphere. If in the data of curve I the substitution $t' = bt$ is made, where $b = 4.9$, it is observed that curve II is nearly reproduced. The quantity $b$ is not quite constant but increases slightly with increasing adsorption. The drift in value of $b$, though small, is nevertheless evident. If one assumes that the rate of adsorption at a given pressure is given by $dS/dt = Kf(S)e^{-E/RT}$, where $S$ is the amount of gas adsorbed, $E$ is the calculated activation energy and $K$ is a kinetic constant, then $E = 20.8$ kcal. when $b = 4.9$. There is, however, a drift in $E$ corresponding to that of $b$, $E$ increasing with increasing adsorption as log $b$ increases. This result corresponds with that of Kohlschütter.[3] A similar small drift is observed when the same calculations are performed on the data of that investigator.

Similar phenomena are observed in the curves obtained at the same temperatures at 0.5 and 0.25 atm. We may thus conclude that, between 491 and 457°K., the energy of activation for the adsorption process is nearly independent of the amount of adsorption within the limits measured, and that the energy of activation is about 21 kcal.

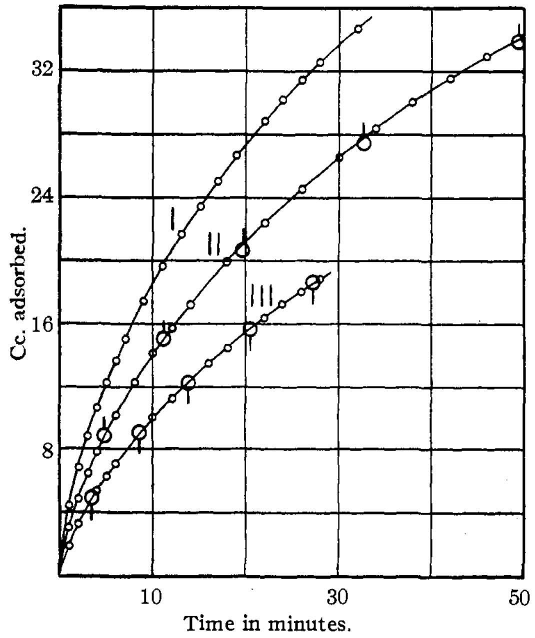

Fig. 2.—Rates of absorption on preparation 9 at 491°K.: I, 1 atm. av. of runs 18 and 19; II, 1/2 atm., av. of runs 28 and 29; III, 1/4 atm. av. of runs 36 and 38; ó I, with subst., $t' = 1.63\ t$; ọ II, with subst., $t' = 1.70\ t$.

**Effect of Pressure.**—Figure 2 represents the data for the adsorption of hydrogen on Preparation 9 at a temperature of 491°K. and pressures of 1, 0.5 and 0.25 atm. It is to be noted that if, in the data for curve I, we substitute $t' = 1.63t$, we reproduce curve II, and if in curve II, for $t$, we substitute $t' = 1.70t$ we reproduce curve III. As it is not possible to average appropriate runs at this temperature, there is an increase in the activity of the preparation as one proceeds from curve I to curve III. If the above values are corrected for this drift, the value of $c$ in $t' = ct$ is about 1.75 in each case.

Qualitatively, then, a change in pressure produces an effect similar to that of a change in temperature. Likewise, the effect of pressure upon the rate of reaction is very nearly independent of the amount of hydrogen adsorbed in these measurements at 491°K. and pressures between 1 and 0.25 atm.

Strother[5] determined the rates of adsorption of hydrogen on ZnO·Mo oxide at 575°K. at 1 and 0.5 atm. pressure. The resulting time–adsorption curves may be treated in the manner outlined above. The value of $c$ so found is 1.66. At higher temperatures such an analysis fails because the rate of desorption has become important.

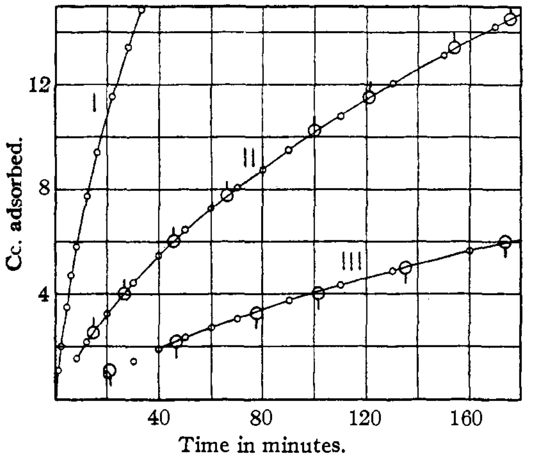

Fig. 3.—Rates of adsorption on preparation 9 at 1 atm.: I, 457°K., av. of runs (23, 25, 34) and 51; II, 427°K., av. of runs (20, 22, 24) and 48; III, 405°K., av. of runs 47 and 49; $\overset{|}{\circ}$ I, with subst., $t' = 5.50\ t$; $\underset{|}{\circ}$ II, with subst., $t' = 3.87\ t$.

**Consideration of the Temperature and Pressure Effects at Lower Temperatures.**—The drift in $b$ discussed previously for the data at 457 and 491°K. becomes much more serious as one proceeds to lower temperatures. Thus, between 457 and 427°K., $b$ increases from 3 at low adsorptions to 5 at high ones. Between 427 and 405°K., $b$ increases from 1 to 3.25. If the curves be taken to represent activated adsorption alone, then between 427 and 405°K. the activation energy at this pressure increases from 0 to 18.5 kcal. as the amount of hydrogen on the surface increases from 1.6 to 8.5 cc. At this pressure and in this temperature range the activation energy of the activated adsorption would not be constant at all. More careful analysis of Kohlschütter's data between 457 and 427°K. reveals a similar variation in the activation energy. Similarly with the data at 427°K. and varying pressures, a serious deviation from constancy becomes evident in $c$, in the equation $t' = ct$, as one reaches lower temperatures. Thus, at 1 and 0.5 atm., $c$ decreases from 4 to 1.8 as the amount of hydrogen adsorbed increases; and at 0.5 and 0.25 atm., $c$ decreases from 5 to 1.95 as the amount of adsorbed hydrogen increases.

The data as a whole thus appear to reveal (a) at higher temperatures, an activated adsorption with an activation energy and a pressure effect nearly independent of the amount of hydrogen adsorbed; and (b) at somewhat lower temperatures, an activation energy and a pressure effect varying markedly with the amount adsorbed.

That any one definite process could be so changed in nature by a rather small change in temperature would be surprising. We will attempt to show that the deviation is but an apparent one, resulting not from a change in the nature of the higher temperature activated adsorption but from the increasing importance at lower temperatures of a process nearly negligible at higher temperatures.

It will be assumed that some process causes the observed adsorptions throughout the greater part of the time–adsorption curve to exceed the adsorptions properly attributable to an adsorption with an activation energy of the order of 21 kcal. by the following amounts at the different temperatures and pressures:

TABLE V

ARBITRARY DEDUCTIONS FROM OBSERVED ADSORPTIONS

| Temp., °K. | Volumes, cc. 1 atm. | 0.5 atm. | 0.25 atm. |
|---|---|---|---|
| 383.5 | 3.15 | | |
| 405 | 2.5 | 1.6 | 1.05 |
| 427 | 1.65 | 1.15 | 0.75 |
| 457 | 1.15 | 0.65 | 0.45 |

In Fig. 3, curves I, II and III were obtained from the corresponding adsorption data as recorded in Table I by subtracting from each adsorption 1.15, 1.65 and 2.5 cc., respectively. It is now observed that if in curve I, the substitution, $t' = 5.50\ t$, is made, curve II is satisfactorily reproduced from the six-minute abscissa on. Similarly curve III is satisfactorily reproduced from the forty-minute abscissa on if the substitution, $t' = 3.87\ t$, is made in curve II.

When the data obtained at 405 and 383.5°K. at one atmosphere are corrected according to the above table and plotted a similar result is obtained. From one hundred and fifty minutes on, *b* is a constant equal to 4.25.

The curves at 0.5 and 0.25 atm. pressure at 405, 427 and 457°K. are amenable to the same treatment and yield the same result.

TABLE VI

CALCULATED VALUES OF *b*

| Temp., °K. | 1 atm. | 0.5 atm. | 0.25 atm. |
|---|---|---|---|
| 383.5 and 405 | 4.25 | | |
| 405 and 427 | 5.50 | 5.39 | 5.50 |
| 427 and 457 | 3.87 | 3.64 | 3.57 |

*b* was a constant in the relation $t' = bt$ after six to eight minutes between 427 and 457°K.; after forty to sixty minutes between 405 and 427°K.; and after one hundred and fifty minutes between 383.5 and 405°K. Any deviations were within the experimental error.

Similar treatment eliminates the slight drift in the value of *b* in Fig. 1. The curve at 457°K., there employed, was not that used above but was necessarily an average of earlier runs. The subtractions appropriate for the curves in Fig. 1, are 0.95 and 0.45 cc. for 457 and 491°K., respectively. The value of *b* which is found is 5.10.

Exactly similar results were obtained with Preparation 10.

The use of the curves thus corrected to give a constant value of *b* in the study of the temperature effect, will give a constant value of *c* in the study of the pressure effect. In Fig. 4, curves I, II and III represent data from Tables I–III from which 1.65, 1.15 and 0.75 cc., respectively, have been subtracted at each pressure.

It is observed that upon performing the substitution, $t' = 1.66\ t$, in curve I, curve II is reproduced. Likewise, the substitution of $t' = 1.81\ t$ in curve II yields curve III. Any deviation is within the experimental error. Similar results are obtained at 457 and 405°K. on Preparation 9. Preparation 10 may be treated in the same fashion. It may be further noted that, as in the investigation of the temperature effect, only that part of the curve representing adsorption at 427°K. lying beyond the eight-minute abscissa is utilizable, and at 405°K., only that part lying beyond the fifty-minute abscissa.

**Rationalization of the Subtraction Process.**—On Preparation No. 9, the adsorption is 17.2 cc. per gram at 82.9°K. and not more than 1.16 cc. per gram at 194.5°K. and 1 atm. pressure. At 273°K. extrapolation to zero time of a still slow adsorption indicates a van der Waals adsorption not exceeding 0.285 cc. per gram. From these data and the variation with pressure, and by comparison with Howard's preparation 1a, similar to ours, we conclude that the van der Waals adsorption at 383.5°K. and 1 atm. cannot exceed 0.013 cc. per gram, or 0.20 cc. for the entire preparation.

At 383.5°K. and 1 atm., 4.7 cc. (of which 0.2 cc. is assigned to van der Waals adsorption) are adsorbed in one hundred and forty minutes. At 491°K. and 1 atm., 4.5 cc. was adsorbed in one For minute. an activation energy of 21 kcal. an adsorption of 4.5 cc. would require five hundred minutes at 383.5°K., on the basis of the observed adsorption at 491°K. In fact, however, this amount is adsorbed in less than one-third of that time. Thus, the adsorption at 383.5°K. must contain some adsorption which is neither van der Waals nor activated adsorption of an activation energy of 21 kcal.

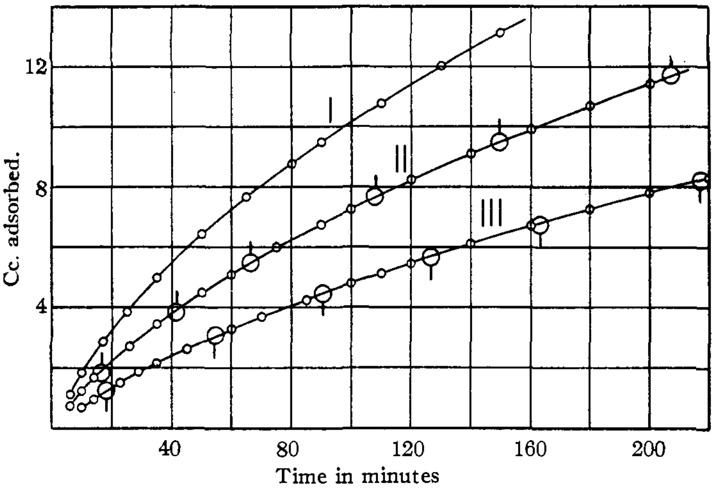

Fig. 4.—Rates of adsorption on preparation 9 at 427°K.: I, 1 atm., av. of runs (20, 22, 24) and 48; II, 0.5 atm., av. of runs (30, 31) and 57; III, 0.25 atm., av. of runs (37, 41) and 45; ȯ I with subst., $t' = 1.66\ t$; ọ II with subst., $t' = 1.81\ t$.

We suggest that the amounts of gas which we have been led to subtract from the observed data in the lower temperature range, 383.5–457°K., represent activated adsorption occurring with lower activation energies than that characterizing substantially all the adsorption above 457°K. Since the amounts subtracted (see Table V) diminish with increasing temperature and decreasing pressure, and since only those sections of the curves after the eight, forty and one hundred and fifty-minute abscissas at 427, 405 and 383.5°K., respectively, are utilizable, we conclude that the subtractions approximate to the equilibrium values of the adsorptions with lower activation energies at the pressures and temperatures indicated. While the subtraction process appears at first sight artificial, careful examination shows that if one subtraction is fixed all of the others are determined by the requirements that $b$ and $c$ be constant. The one which is arbitrarily fixed is that which renders the curves at 457°K. and 1 atm. homogeneous and of zero adsorption at zero time, *i. e.*, van der Waals adsorption immeasurably small.

Assuming the subtracted amounts to be equilibrium values for adsorption with activation energy less than 21 kcal. it is possible to make a rough calculation of the heat of adsorption of the process. The heat so calculated is of the order of 10 kcal. in marked contrast to that found earlier[4] for the higher temperature adsorption, $\lambda = 27$ kcal.

Taylor and Strother demonstrated, with zinc oxide, the existence at lower temperatures (0–110°) of activated adsorption with lower activation energies than those measured in a higher temperature range. On that adsorbent the adsorption occurring with the lower activation energies had already begun to decrease with increasing temperature before the adsorption with higher activation energies had set in to any marked extent. The data also point to a lower heat of adsorption for the process with the lower activation energy, as in the present observations with chromic oxide. Emmett and Harkness[6] find similar phenomena with iron synthetic ammonia catalysts and Morozov[7] reported results on pure iron similar to those of Emmett and Harkness although he interprets the high temperature process as diffusion.

We now recall the observations of Gould, Bleakney and Taylor[8] that chromic oxide gel of this type is an excellent catalyst for the reaction $H_2 + D_2 = 2HD$ in the range from 83 to 273°K. From such results it follows that since equilibrium in the gas phase in this reaction is readily established in this temperature range the processes of activated adsorption of reactants and desorption of products must occur readily and that the energies and heats of activated adsorption involved in such processes must be quite small, no larger than a few kilocalories at most.

We therefore envisage the chromic oxide surface as one having essentially a continuum of activation energies of hydrogen adsorption from quite low values to a surface area fairly uniform and relatively large in extent having an activation energy of 21 kcal. The evidence indicates also that the areas with lower activation energies have in general lower heats of adsorption than those of highest activation energy. Surfaces active in very low temperature processes ($\sim$ 83°K.) must possess both low activation energies and low heats of adsorption. These areas will be substantially bare and of relatively little importance catalytically in the high temperature ranges.

An experiment at 353°K. and 1 atm. pressure confirms our deduction of areas with low heats and energies of activated adsorption. On a freshly evacuated surface under the given conditions 1.85 cc. was adsorbed in the first two minutes. In the next twenty-eight minutes 0.8 cc. was adsorbed. After one hundred and eighty minutes the rate of adsorption was 0.075 cc. in twenty minutes. After 180 minutes the system was pumped out for twenty-five minutes at the same temperature. The run was then restarted. It was then observed that the adsorption in two minutes was 1.65 cc. and that, in a further twenty-eight minutes, 0.4 cc. was adsorbed. Similar results were obtained in experiments at 0.5 atm. pressure.

**General Considerations of the Form of Temperature and Pressure Effects.**—The analysis made in the preceding discussion leads us to the conclusion that we can thus separate from the total observed adsorption, an adsorption occurring on a reasonably uniform surface over a range of temperature and pressure. We are thus encouraged to examine more closely the form of effects produced by these two variables.

Let it be assumed that we can represent the rate of adsorption $\mathrm{d}S/\mathrm{d}t$ in a general manner by the expression, $\mathrm{d}S/\mathrm{d}t = \mathrm{f}(p)\mathrm{f}'(T)\mathrm{f}''(S)$, where f, f′, f″ are functions to be ascertained of pressure, temperature and surface $S$. From this expression it follows that

$$\int_0^S \frac{\mathrm{d}S}{\mathrm{f}''(S)} = \mathrm{f}(p)\mathrm{f}'(T)\int_0^t \mathrm{d}t + C$$

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[6] Emmett and Harkness, This Journal, **57**, 1631 (1935).

[7] Morozov, *Trans. Faraday Soc.*, **31**, 659 (1935).

[8] Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

where $C = 0$ if $S = 0$ when $t = 0$. By integration

$$\mathrm{F}(S) = \mathrm{f}(p)\mathrm{f}'(T)t$$

At two temperatures $T'$ and $T''$, we know that $\mathrm{f}'(T') = b\mathrm{f}'(T'')$ where $b$ is a constant. Further

$$\begin{aligned} \mathrm{F}(S') &= b\mathrm{f}(p)\mathrm{f}'(T'')t' \\ \text{and } \mathrm{F}(S'') &= \mathrm{f}(p)\mathrm{f}'(T'')t'' \end{aligned}$$

whence if $S' = S''$, $t'' = bt'$. This relation of times has been shown in the preceding to be valid in the pressure, temperature and adsorption range for our data adjusted by the subtraction process.

The simplest assumption to make as to the form of $\mathrm{f}'(T)$ is that $\mathrm{f}'(T) = e^{-E/RT}$ where $E$ is the activation energy. If $e^{-E/RT'} = be^{-E/RT''}$ then

$$E = \frac{RT'T''}{T - T''} \log b$$

Using this relation, $E$ has been calculated between certain temperatures at 1, 0.5 and 0.25 atm. with the adjusted data from Preparation No. 9. The results are presented in Table VII.

TABLE VII

CALCULATED ACTIVATION ENERGIES ON FRACTIONAL SURFACE OF CHROMIC OXIDE GEL

| Temp., °K. | Pressures, atm. 1.0 | 0.5 | 0.25 |
|---|---|---|---|
| 491–457 | 21.4 | 21.6 | 21.9 |
| 457–427 | 22.1 | 21.8 | 22.1 |
| 427–405 | 21.2 | 20.3 | 20.0 |
| 405–383.5 | 21.0 | | |

We conclude that an expression of $\mathrm{f}'(T) = e^{-21,700/RT}$ represents the adjusted data satisfactorily between 427 and 491°K., without dependence on the operating pressure. On Preparation No. 10, an $E = 21{,}500$ cal. represents equally well the adjusted data between 405 and 457°K. With Preparation No. 6 the data gave $E = 22{,}800$ cal.

The separability of the functions of $S$ and $p$ may be tested similarly. At constant temperature we write

$$\begin{aligned} \mathrm{f}(p') &= c\mathrm{f}(p'') \\ \text{and} \quad \mathrm{F}(S') &= c\mathrm{f}(p'')\mathrm{f}'(T)t' \\ \mathrm{F}(S'') &= \mathrm{f}(p'')\mathrm{f}'(T)t'' \end{aligned}$$

where $c$ is a constant. Thus for $S' = S''$, $t'' = ct'$. This relation has also been shown valid for the adjusted data.

In Table VIII we present data indicating the form of $\mathrm{f}(p)$, as applied to Preparation No. 10 from 1 to 0.125 atm. at 457°K., $\mathrm{f}(p)$ obsd. being set equal to unity at 1 atm. pressure. The values at lower pressures are determined from the observed values of $c$.

TABLE VIII

EFFECT OF PRESSURE ON THE RATE OF ADSORPTION ON FRACTIONAL SURFACE OF CHROMIC OXIDE GEL, NO. 10, AT 457°K.

| Pressure, mm. | $\mathrm{f}(p)$obsd. | $(p/758)^{0.818}$ | $\frac{1.418(p/758)}{1 + 0.418(p/758)}$ |
|---|---|---|---|
| 758 | 1.00 | 1.00 | 1.00 |
| 382.5 | 0.572 | 0.572 | 0.590 |
| 192 | .325 | .325 | .325 |
| 92.5 | .178 | .179 | .165 |

Similar data on Preparation No. 9 are equally well represented by expression of the form $p^n$ and $p/(1 + ap)$. At the higher temperatures, the measurements seem to be better represented by $p^n$; $p/(1 + ap)$ appears to be more serviceable at the lower end of our temperature range. In a restricted pressure range it is obvious that the two expressions are substantially equivalent. We attach significance, however, to the conclusion that the functions of pressure found applicable are those which characterize the variation of amount of adsorbed gas on a surface rather than the external gas pressure.

**The Surface Factor.**—Attempts to estimate the influence of surface covered on the velocity of adsorption have generally been complicated hitherto by the non-uniformity of the surface as revealed by varying activation energies. The present data as experimentally received at 457 and 491°K. or at lower temperatures as amended by the processes of calculation set forth in the preceding offer the possibility of examining the surface factor on a sensibly uniform surface. The data of Benton and Drake[9] for oxygen on silver appear to apply to a uniform surface, but the gas volumes (2.4 and 5.8 cc.) on which measurements were available were small. From them and his own data Roginsky[10] concludes the general validity of the equation $\mathrm{d}S/\mathrm{d}t = ce^{-\alpha S}$. This equation has been tested against the data of this paper and has been found incompatible with them. It is evident that the reason for this lies in the relatively very small change in rate of adsorption on chromic oxide gel with increased covering of the surface. Thus, on Preparation No. 9 at 491°K., the adsorption from the second to the third minute was 2.05 cc., with 7–9 cc. adsorbed. After the adsorption of 52 cc. ($t = 120$) the rate of adsorption is still 0.05 cc. This 40-fold variation in velocity which represents our greatest velocity variation with surface covered is to be contrasted with a

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[9] Benton and Drake, THIS JOURNAL, **56**, 255 (1934).

[10] Roginsky, *Acta Phys.-Chem. U. S. S. R.*, **1**, 664 (1934).

$10^5$-fold variation with Benton and Drake between adsorption of 1 and 2.4 cc. of oxygen on silver.

An equation tested by Howard[11] of the form $S = at^{\mathrm{m}}$ applies to our data over a quite limited range but deviates increasingly with increased adsorption. If changed into the form $\sigma \log \sigma/(\sigma - S) = at^{\mathrm{m}}$, used by Burt, Bangham and co-workers,[12] which, for small values of $S$ is identical with $S = at^{\mathrm{m}}$, satisfactory agreement with the experimental data can be obtained with reasonable values for $\sigma$, which is to be identified with the saturation value of the adsorption.

We do not attach much importance to such empirical expressions. We believe that we can account reasonably for the 40-fold variation in adsorption velocity, during the adsorption of 53 cc. at 491°K., on the assumptions that the decrease is due (a) to exhaustion of available adsorbing surface, (b) decrease in van der Waals adsorption due to increasing activated adsorption. On this view, we ascribe the activated adsorption to interaction between van der Waals adsorbed gas and a surface which receives the activation energy necessary to transformation of the van der Waals to activated adsorption. Our data on volumes adsorbed in protracted rate runs indicate that, with 53 cc. adsorbed, the surface is more than three-quarters covered. If, as is reasonable from Howard's data[11] on the influence of activated on van der Waals adsorption, we assume that, at high coverage, the latter type of adsorption is reduced to one-fifth or one-sixth of its value in the absence of activated adsorption, then the change in velocity of adsorption still to be accounted for lies well within the range of uniformity of surface postulated. About 1 kcal. change in activation energy would account for all the discrepancy. Our data then can be expressed in terms of the equation

$$\mathrm{d}S/\mathrm{d}t = ke^{-21.7/RT}\, p^{0.8}\, (1 - \theta)\mathrm{f}(\theta)$$

where $(1-\theta)$ expresses the surface still bare and $\mathrm{f}(\theta)$ is the factor which accounts for change in van der Waals adsorption with increased activated adsorption. It is impossible to state whether the large variation in velocity found by Benton and Drake can be similarly interpreted. The majority of the variation would have to be ascribed to the $(1-\theta)$ term. It is significant that these authors found the greatest variation in velocity ($10^5$) with a surface of small capacity (0–2.4 cc. adsorbed) whereas with the surface of larger capacity the variation in velocity from 0–5 cc. adsorption was only 100-fold.

It should be observed that the mechanism of activated adsorption which we here postulate, the slow process being a reaction between surface atoms which receive the necessary activation energy and hydrogen molecules adsorbed by van der Waals forces, is in accord with the observations that hydrogen and deuterium are adsorbed under such experimental conditions at the same rates. This does not exclude that under other conditions of surface, and especially of pressure, other factors determining rate would assume importance. It is obvious, for example, that at very low gas pressures the velocities of the hydrogen and deuterium molecules must enter as factors of importance. Our studies of the pressure factor in the range 0.25–1 atm. are in entire agreement with the observations made previously as to the relative velocities of adsorption of hydrogen and deuterium at atmospheric pressure. The detailed mechanism of activated adsorption which has been described may, as Professor Eyring has pointed out to us, be more generally described by an equation applicable to a rate of adsorption at constant temperature and pressure analogous to that developed by Bjerrum and Brönsted for homogeneous reactions

$$\mathrm{d}x/\mathrm{d}t = k\, \frac{\mathrm{f}_{\mathrm{H}_2}\, \mathrm{f(surface)}}{\mathrm{f}_{\mathrm{act.}}}\, [\mathrm{H}_2]\, [\mathrm{surface}]$$

The behavior which we seek to explain in terms of interaction of molecules adsorbed by van der Waals forces with a surface receiving activation energy would in such an equation find its interpretation in the changing values of the activity coefficient of gas, surface and activated complex.

## Summary

1. Rates of adsorption of hydrogen on several varieties of chromic oxide gel have been determined at temperatures from 195 to 491°K. and at pressures from 0.125 to 1 atmosphere.

2. Analysis of the data leads to the conclusion that the surface of chromic oxide gel is composite, with areas having characteristic activation energies of hydrogen adsorption ranging from low values to a value of 21.7 kcal. per mole. This latter obtains on an area relatively uniform and large in extent.

3. The influence of temperature, pressure and occupied surface on the velocity of adsorption on the uniform area has been studied.

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(11) Howard, Thesis, Princeton, 1933.

(12) Bangham and Stafford, *J. Chem. Soc.*, **127**, 1085 (1925); Bangham and Burt, *J. Phys. Chem.*, **29**, 115, 119 (1925).

4. The data lead to the conclusion that the slow process of adsorption may be described as an interaction between molecules adsorbed by van der Waals forces and surface atoms which receive the necessary activation energy.

5. Such a process is in accord with previous observations on the velocities of adsorption of hydrogen and deuterium at atmospheric pressure on chromic oxide gel in the same temperature range.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

# A Kinetic Correlation of Two Reactions Involving Hydrogen Peroxide. Its Oxidations by "Chloramine T" and by Chlorine

BY HERMAN A. LIEBHAFSKY

Although the use of "chloramine T," $TSO_2NClNa$,[1] as an analytical reagent is no longer new,[2] the kinetics of reactions involving this interesting oxidizing agent (or similar nitrogen compounds) have not been extensively investigated. Coull, Hope and Gouguell[3] have recently measured the rate at which hydrogen peroxide is oxidized in 0.15 *M* hydrochloric acid solutions containing "chloramine T" at concentrations near 0.006 *M*. They conclude that chlorine reacts directly with the peroxide and that "it becomes necessary. . .to designate the 'chloramine T' entering the reaction as 'active'." We shall show that a satisfactory mechanism for the stoichiometric reaction

$$TSO_2NHCl + H_2O_2 = TSO_2NH_2 + H^+ + Cl^- + O_2 \quad (1)$$

can be formulated without their assumption of an "active" species, and that their results agree with those of Makower and Bray[4] for the reaction

$$Cl_2 + H_2O_2 = 2H^+ + 2Cl^- + O_2 \quad (2)$$

When $TSO_2NClNa$ is dissolved in water, the hydrolysis equilibrium

$$TSO_2NCl^- + H_2O \rightleftarrows TSO_2NHCl + OH^- \quad (3)$$

will be rapidly established; presumably $TSO_2ClH$ is a weak acid, so that we may expect a small, but appreciable, fraction of its anion to be hydrolyzed. When such a solution is acidified, the stoichiometric reaction

$$TSO_2NCl^- + H^+ = TSO_2NHCl \quad (4)$$

occurs. The chemistry of $TSO_2NHCl$ and similar compounds is consistent with the assumption that these substances in aqueous solution are in rapid equilibrium with hypochlorous acid and, if hydrochloric acid is present, with chlorine; thus

$$TSO_2NHCl + H_2O \rightleftarrows TSO_2NH_2 + HClO \quad (5a)$$

$$TSO_2NHCl + H^+ + Cl^- \overset{K_5}{\rightleftarrows} TSO_2NH_2 + Cl_2 \quad (5)$$

Since the hydrolysis equilibrium of chlorine

$$Cl_2 + HO_2 \overset{K_6}{\rightleftarrows} HClO + H^+ + Cl^- \quad (6)$$

is always maintained in an aqueous hydrochloric acid solution, Equilibria 5a and 5 are alternative ways of describing the experimental fact that an acid $TSO_2NClNa$ solution contains "free" chlorine ($HClO$ or $Cl_2$) in equilibrium amount.

The experimental results of Coull, Hope and Gouguell will now be interpreted by assuming that Equilibria 5a, 5 and 6 are always maintained in reaction mixtures prepared by adding hydrochloric acid to aqueous solutions of $TSO_2NClNa$ and $H_2O_2$, and that the rate of Reaction 1 is equal to the rate at which Reaction 2 proceeds. In dilute hydrochloric acid solution the rate of Reaction 2 (specific rate, $\chi_2$) is given by

$$-d(H_2O_2)/dt = \chi_2 \frac{(Cl_2)}{(H^+)(Cl^-)(\gamma_\pm)^2}(H_2O_2) \quad (2a)$$

With Equilibrium 5 maintained

$$(Cl_2) \doteq K_5(TSO_2NHCl)\ (H^+)\ (Cl^-)\ (\gamma_\pm)^2/(TSO_2NH_2)$$

therefore

$$-d(H_2O_2)/dt = \chi_2 K_5 \frac{(TSO_2NHCl)}{(TSO_2NH_2)}(H_2O_2) = k\frac{(TSO_2NHCl)}{(TSO_2NH_2)}(H_2O_2) \quad (1a)$$

The simple expression on the right, to which our rate law leads, becomes identical with that employed by Coull, Hope and Gouguell to explain the rate law of Reaction 1 if we grant that ($TSO_2NHCl$) is roughly 90% that formed from the "chloramine T" initially added. They assumed that this 90% is "active," but an active species does not usually constitute so large a proportion

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(1) "T" in the formula of a compound will represent the *p*-toluyl radical. For the other abbreviations and conventions, see ref. 5, p. 90.

(2) (a) Noll, *Chem. Zeit.*, **48**, 845 (1924); *cf.* (b) Komarowsky, Filonowa and Korenman, *Z. anal. Chem.*, **96**, 321 (1934).

(3) Coull, Hope and Gouguell, THIS JOURNAL, **57**, 1489 (1935).

(4) (a) Makower and Bray, *ibid.*, **55**, 4765 (1933); (b) Makower, *ibid.*, **56**, 1315 (1934).