vanced arises from the thermodynamic consideration that in such a case the rate of thermal dissociation of chlorine molecules should also be accelerated by water vapor.

Summary

1. A brief account of theories on the nature of the primary photochemical process in chlorine has been given.

2. Earlier measurements and the data now obtained show that extreme drying of chlorine does not change appreciably either the structure of its absorption spectrum or the total amount of light energy absorbed.

3. Measurements of a possible fluorescence in dry chlorine reveal that certainly less than 5% of the absorbed light energy is reëmitted as fluorescence.

4. It has been suggested, in order to reconcile these experimental results with the known influence of moisture on the Budde effect, that chlorine (or other halogen) is dissociated into atoms on absorption of light energy in the region of continuous absorption independently of its degree of purity; water is assumed to have a catalytic influence on the rate of recombination of the atoms and, therefore, also on the rate of thermal dissociation of chlorine molecules.

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[Contribution from the Laboratory of Physical Chemistry, Princeton University]

HEATS OF ADSORPTION ON POISONED AND HEAT-TREATED CATALYSTS

By George B. Kistiakowsky,[1] Earl W. Flosdorf and Hugh S. Taylor

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In the preceding five years the non-uniform character of the catalyst surface has been developed by quantitative studies of adsorption, reaction kinetics, poisoning and promoter action on a variety of catalysts. This differentiation in the catalytic activities of the units in the catalyst surface has permitted an experimental attack on the problem of activation at the catalyst surface, a most important step in placing the study of contact catalysis on a scientific basis and in freeing catalysis from the bane of empiricism.

Experiments by Gauger[2] and by Wolfenden[3] on the ionization potentials of adsorbed hydrogen on hydrogenation catalysts have indicated that the hydrogen adsorbed on the more active portions of a catalyst surface may be atomic. These experiments were extended by Kistiakowsky[4]

[1] International Research Fellow.

[2] Gauger, This Journal, **46**, 674 (1924).

[3] Wolfenden, *Proc. Roy. Soc.* (London), **110A**, 404 (1926).

[4] Kistiakowsky, *J. Phys. Chem.*, **30**, 1356 (1926).

to ammonia-making catalysts, with the result that evidence for the presence of both atomic nitrogen and hydrogen was obtained. A series of investigations with the problem of activation as the objective is also in progress in Princeton, the heat of adsorption of the gas being the measure of activation. The work of Beebe and Taylor[5] showed that the integral heat of adsorption of hydrogen on nickel and copper was of the order of 10,000–20,000 calories, greatly in excess of the heat of liquefaction, and variable with varying preparations of catalyst. Fryling[6] elucidated this variable behavior by a study of promoted nickel catalysts, showing, in addition, that on active promoted catalysts the curve for the heat of adsorption with increasing adsorption gave initially low values, next a maximum and then decreasing heats of adsorption. Fryling attributed the initial rise in the curve to an activation of the adsorbed hydrogen molecules, the heat measured being a composite of a positive heat of adsorption and a negative heat of activation. Fryling assumed that, in the limit, this activation consisted in a dissociation into hydrogen atoms.

As pointed out by Taylor,[7] on the assumption of a dissociation into atoms, from the initial heat of adsorption at very low partial pressures a value of the heat of adsorption of hydrogen atoms can be deduced and hence a more penetrating analysis of the possible stages in a contact catalytic hydrogenation or dehydrogenation process may be secured. To study these limiting values of adsorption heats a more exact experimental technique has been developed[8] which permits the measurement of the heat of adsorption of a few tenths of a cc. of gas on 100 g. of a catalyst. We have reported the results of such a study elsewhere, using a sample of reduced copper as adsorbent and both hydrogen and carbon monoxide as adsorbates. In the case of hydrogen, an active catalyst and one poisoned with oxygen were studied. The active catalyst showed a maximum in the curve similar to that reported by Fryling on nickel. Poisoning the catalyst with oxygen eliminated this maximum. In the case of carbon monoxide as adsorbate, the initial gas adsorbed showed high values, which fell as adsorption proceeded to a minimum value, the amount there adsorbed corresponding identically to the position on the hydrogen curve where a maximum was shown. The carbon monoxide heat of adsorption then showed a further increase to a maximum and subsequently a steady decrease. Kistiakowsky has shown[9] that all these results are in agreement with a modified Langmuir theory of gas adsorption in which the surface shows varying types of "elementary spaces"

[5] Beebe and Taylor, This Journal, **46**, 43 (1924).

[6] Fryling, *J. Phys. Chem.*, **30**, 818 (1926).

[7] Taylor, *Proc. Roy. Soc.* (*London*), **113A**, 77 (1926).

[8] Taylor and Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927).

[9] Kistiakowsky, *Proc. Nat. Acad. Sci.*, **13**, 1 (1927).

on some of which activation as well as adsorption of the gas molecules can occur, whereas on the remainder adsorption alone occurs.

Earlier studies of metallic catalysts[10] have shown that their sensitivity to heat treatment was much more pronounced when catalytic activity instead of adsorptive capacity was used as the criterion of sensitivity. Thus, Pease showed that a 70% decrease in hydrogen adsorptive capacity and a 22% decrease in ethylene adsorptive capacity, at 1 atmosphere, were accompanied by a decrease in catalytic activity amounting to 85%. Such results pointed to the importance, for catalytic activity, of the strong or low-pressure adsorption, a conclusion which the poisoning studies abundantly confirmed. The new technique now available for measurement of heats of adsorption of small amounts of gas at very low partial pressures permits a reëxamination of the problem from the standpoint of heats of adsorption, and yields, as is shown in the following pages, abundant confirmation of this conclusion and a further development of our ideas concerning activation in its dependence on the nature of the catalyst surface. We have examined the heats of adsorption of hydrogen on an active copper catalyst and on the same catalyst after two successive reductions in activity by suitable heat treatment. For purposes of comparison we also record our earlier results with poisoned copper.

Experimental

The heats of adsorption were measured in a special glass vacuum calorimeter which has already been described in detail elsewhere.[11] The apparatus used in these studies was unchanged save that the dead space in the apparatus outside the calorimeter was still further reduced with the object of increasing the accuracy of the adsorption measurements. We do not, however, estimate the accuracy any higher than that previously claimed, namely, 10%; on the most important portions of the curves, below 3 cc. of adsorbed gas, we believe the accuracy is higher than this. But a 10% accuracy is adequate for all the conclusions that we shall draw from the results. In the earlier work we may have overestimated the accuracy of the measurements at the end of the curve where 80% of the gas admitted is not adsorbed. Since this part of the curve (> 8 cc. adsorbed) is not of interest in the present study, we have not pursued the measurements in this region with sufficient care to state any definitive results. The details of the measurement of heats of adsorption, extent of adsorption and of the heat capacity of the calorimeter have already been given[12] and will not be repeated here.

Catalysts Employed.—Measurements have been made on a sample of copper obtained by reduction of a high grade of copper oxide granules.

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[10] Pease, This Journal, 45, 2296 (1923).

[11] Ref. 8, p. 352.

[12] Ref. 8, p. 353.

The reduction was carried out very slowly with hydrogen gas at a temperature of 160° over a period of weeks, and gave us a sample (No. 1) of high catalytic activity and adsorptive capacity. To obtain the less active preparations this catalyst was subjected subsequently to two successive heat treatments, the first at 250° for 30 hours in a vacuum, the second to 300° for a period of 8 hours. The sample after these two treatments is designated as No. 2 and No. 3 in the experimental results. On the catalyst in each state, measurements were made of the heat of adsorption of successive increments of 0.3-0.4 cc. of hydrogen up to 8 cc. adsorbed.

Experimental Results.—The experimental data thus secured are shown graphically in Figs. 1 and 2. In Fig. 1 are recorded all the experimental data on the heats of adsorption of the catalyst in its three states of preparation. Fig. 2 records the pressure and adsorbed amount before and after the first heat treatment.

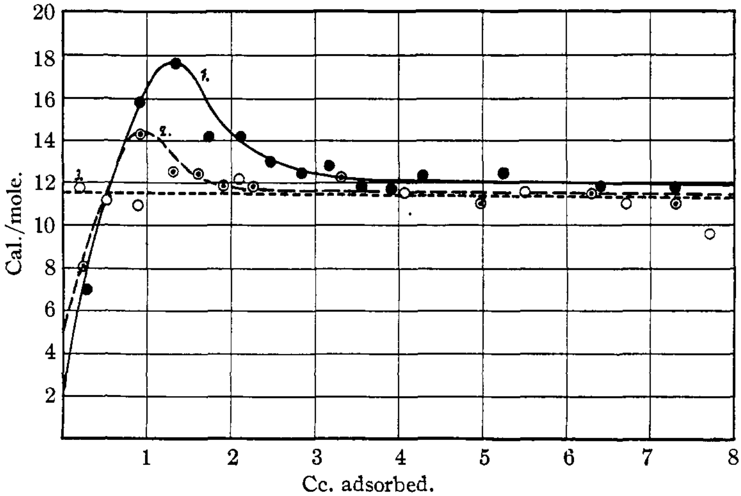

Fig. 1.—Heat treatment. 1.—● 160°; 2.—◉ 250° (30 hrs.); 3.—○ 300° (8 hrs.).

In regard to heats of adsorption, the experimental results are exactly what would be expected from our previous experience with such catalysts and from the theory of the catalytic surface developed in Princeton. The most active preparation (Fig. 1, No. 1) shows the most pronounced maximum in the curve and a maximum at a point corresponding to 1.5 cc. of adsorbed gas. The first heat treatment reduces the heat developed at the maximum and also decreases the amount adsorbed at the maximum to 1 cc. The second heat treatment eliminates all evidence of a maximum. We interpret these results as indicating in the active preparations a greater fraction of the surface capable of activating the adsorbed species, the activation process being endothermic and, possibly, a dissociation into atoms. The heat treatment destroys these active areas on the surface preferentially.

That the destruction of these areas may be without marked influence on the *total* adsorption is evident from Fig. 2. The curves show that the pressure at which a small amount of gas is adsorbed is markedly less with the active preparation (1) than with the heat-treated catalyst (3).

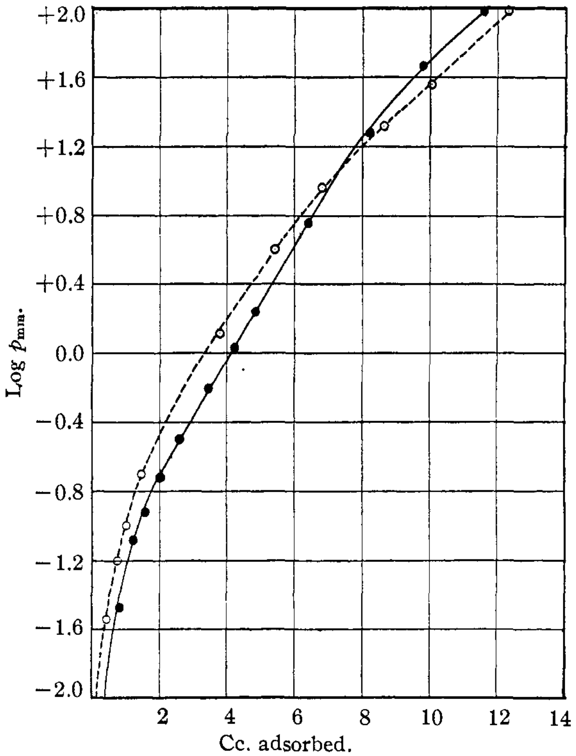

Fig. 2.—Pressure and adsorbed amount before and after heat treatment.

Heat treatment destroys the surface which adsorbs at low pressures. Beyond 8 cc. of adsorbed gas, however, the curves cross each other and, in this case at least, the heat-treated catalyst displays in the region 8–12 cc. adsorbed (20–100 mm. pressure), a higher adsorption at a given pressure. It is possible, however, that these curves might again cross each other at higher gas pressures. Our experimental set-up in this study was not suited to such measurements, but other data in this Laboratory suggest its probability. We see in such complex adsorption isotherms the best possible evidence of a surface of "variable elementary spaces," the distribution of which may vary widely between the extremes of most active and least active.

In Fig. 3 we record the results of an earlier study of an active copper catalyst before and after poisoning with oxygen. The active catalyst (No. 1) is seen to be in every way similar to that in Fig. 1; the poisoning with oxygen destroys the maximum in the curve and gives a curve (No. 2) which we regard as typical of adsorption without activation. This is in accord with our concept that poisons are preferentially adsorbed on the active areas.

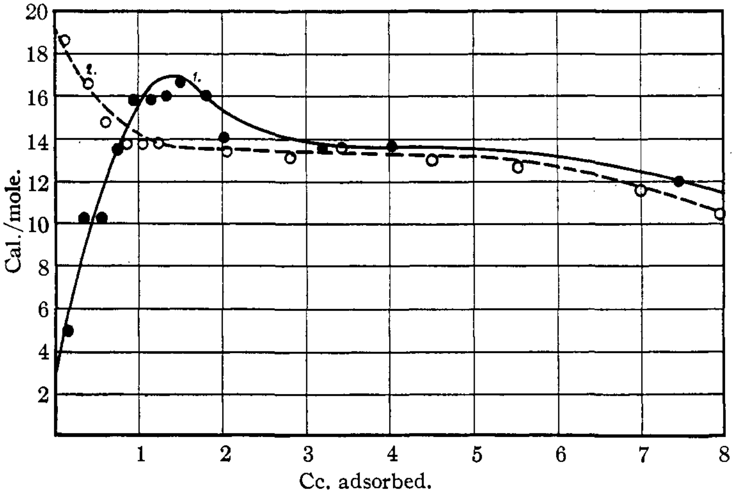

Fig 3.—Oxygen treatment.

Theoretical

A difficulty of theoretical importance in connection with these results on the heat of adsorption on active catalysts may now be stated in the hope that some suggestions may be forthcoming as to its solution. It has been pointed out to us by Professor K. Herzfeld of Johns Hopkins University that, with the active preparations, the process first occurring is one in which the decrease in internal energy is very much less than that occurring subsequently at the maximum point and beyond. There is no evidence that the entropy changes involved would cause the free energy decrease at low absorptions to be greater than those obtaining at the maximum. The problem therefore arises as to why the process with a smaller free energy decrease should occur preferentially to that in which the larger free energy decrease can take place. It is known, of course, that change in free energy is not a measure of reaction velocity in many chemical reactions. Does the same hold true in processes of adsorption?

Summary

Measurements of the heat of adsorption of hydrogen on active and heat-treated copper catalysts have been made.

The active preparations show maxima in the curves of heat of adsorption plotted against amount adsorbed.

With partially de-activated catalysts the maximum occurs when smaller amounts of gas are adsorbed. Further de-activation eliminates such maxima.

These results are in harmony with a theory of the catalytic surface with variable elementary spaces, upon the most active of which adsorption is accompanied by an endothermic activation process.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA

BY CHARLES A. KRAUS, E. SEATON CARNEY AND WARREN C. JOHNSON

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According to Kraus and Lucasse[1] the density of a concentrated solution of sodium or potassium in liquid ammonia is markedly lower than that of either of its components, which shows that the process of solution of these metals is accompanied by a large increase in volume. Forney[2] investigated the density of solutions of sodium in liquid ammonia at higher concentrations, using for this purpose a specially designed spring balance. This method, however, did not prove sufficiently sensitive to admit of accurate determination of the volume change. Since these solutions are very exceptional in their behavior, it was thought worth while to develop a method whereby their density could be determined with a relatively high degree of accuracy. An apparatus was therefore designed whereby the density was measured directly by means of a Westphal balance.

Apparatus and Procedure

The chief difficulty encountered in determining the density of solutions of the alkali metals in liquid ammonia is due to their extreme reactivity toward oxygen and moisture. This was overcome by maintaining an atmosphere of hydrogen over the solutions during the course of the measurements. The essential features of the apparatus are shown in outline in Fig. 1. The balance, which was equipped with suitable clamping and leveling devices, was placed in a sealed case provided with plate glass windows on opposite sides. Special riders were constructed of inverted "U" form, carrying a loop at the top. The riders were manipulated

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[1] (a) Kraus and Lucasse, THIS JOURNAL, **43**, 2538 (1921); (b) *ibid.*, **44**, 1941 (1922).

[2] Forney, *Thesis*, Clark University, **1923**.