25°. Using the value -0.2800 v.[5,14] for the normal calomel electrode, we obtain for Ag(s), Ag_2CrO_4(s), 0.1 N $CrO_4{}^=$ the value $E = -0.507$ v. This is in good agreement with our value of -0.5050 v. Next, calculating the value of E^0 from Abegg and Cox's results, we obtain -0.448 which again agrees with our value of -0.4463.

Bolam and MacKenzie[2] measured the cell Ag, $AgNO_3$(0.1 N), NH_4OH(10 N), K_2CrO_4(0.1 N), Ag_2CrO_4, Ag and obtained the value 0.2247 v. Lewis[15] found $E = -0.399$ v. for the cell Ag, $AgNO_3$(0.1 M), KNO_3(0.1 M), KCl(0.1 M) Hg_2Cl_2, Hg. Noyes and Brann[16] found for this same cell $E = -0.3992$ v. Lewis and Randall,[9] (p. 414) on the basis of these results, corrected for the liquid junction and obtained $E = -0.3985$ v. Since the value of the decinormal calomel electrode is -0.3351 v., we thus obtain for Ag(s), Ag_2CrO_4(s), $CrO_4 =$ (0.1 N) the value $E = -0.5089$ v. This gives $E^0 = -0.4504$ v.

The standard electrode potential calculated from the data of Hass and Jellinek[2] is $E^0 = -0.462$ v.

The change in free energy for the reaction

$$Ag_2CrO_4(s) \longrightarrow 2Ag^+ + CrO_4{}^=$$

may be calculated from the solubility product as well as from the standard electrode potentials. Values calculated from various data are summarized in Table IV. Hass and Jellinek[2] measured the potential of the silver–silver chromate electrode in order to calculate the activity coefficients of the chromate ion. Their values, compared with ours, are listed in Table IV.

TABLE IV

Investigator	E^0, v.	K s. p.	ΔF^0 $Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4{}^=$ cal.
Hass and Jellinek[2]	-0.462		15,576
Bolam and MacKenzie[2]	$-$ .4504		16,111
Abegg and Cox[2]	$-$ .448		16,222
Cann and Mueller	$-$ .4463		16,300
Abegg and Shäfer[a]		2.64×10^{-12}	15,803
Kohlrausch[b]		4.05×10^{-12}	15,550
Sherrill[c]		9.0×10^{-12}	15,077

[a] *Z. anorg. Chem.*, **45**, 293 (1905).
[b] *Z. physik. Chem.*, **64**, 149 (1908).
[c] THIS JOURNAL, **29**, 1641 (1907).

The variation in these values may be due to the fact that electrolytic silver chromate was used in the present work, whereas Hass and Jellinek used the precipitated salt. The thermodynamic properties of substances prepared by dissimilar methods may be very different.

Summary

The cell Ag(s), Ag_2CrO_4(s), K_2CrO_4(aq), KCl(aq), AgCl(s), Ag(s) was investigated.

The normal electrode potential of Ag(s), Ag_2CrO_4(s), $CrO_4{}^=$ was found to be $E^0 = -0.4463$ v.; $\Delta F^0 = 20{,}596$ cal.

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[14] Spencer, THIS JOURNAL, **54**, 3649 (1932).

[15] Lewis, *ibid.*, **28**, 158 (1906).

[16] Noyes and Brann, *ibid.*, **34**, 1016 (1912); Bray and Hershey, *ibid.*, **56**, 1891 (1934).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Adsorption of Hydrogen and Deuterium on Copper at Low Pressures[1]

BY RALPH A. BEEBE, GEORGE W. LOW, JR., EDWIN LINCOLN WILDNER AND SEYMORE GOLDWASSER

Attention has been called by Pace and Taylor[2] to the fundamental importance which is attached to experimental studies of the relative velocities of the activated adsorption of hydrogen and deuterium on catalytically active surfaces. These authors have found no difference in the rates of adsorption for the two isotopes on the hydrogenating catalysts chromium oxide, zinc oxide–chromium oxide and nickel at one atmosphere pressure and over the temperature range 110–184°. This observation was unexpected because, on account of the difference in zero point energies, the activation energy should be greater for deuterium than for hydrogen, and the rate of adsorption correspondingly less for deuterium.

More recently direct experimental evidence has been presented by Klar,[3] and indirect evidence based upon the interpretation of the rates of catalytic reactions has been presented independently by Klar,[4] and by Fajans[5] to show very definite differences in the adsorption of the two hydrogen isotopes on active nickel.

Because of the apparent discordance among the

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[1] Presented before the Division of Physical and Inorganic Chemistry at the ninety-first meeting of the American Chemical Society held in New York City on April 22–26, 1935.

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

[3] R. Klar, *Naturwiss.*, **22**, 822 (1934).

[4] R. Klar, *Z. physik. Chem.*, **27B**, 319 (1935).

[5] E. Fajans, *ibid.*, **28B**, 239 (1935).

results which have been described above, it seems advisable at this time to present our data on the adsorption of the two gases by copper, although we feel that more detailed experimental work will be needed before a satisfactory explanation of all our results will be possible. Our measurements have extended over the temperature range −78 to 125° and the pressure interval, 0 to 2 mm. In agreement with Klar's work we have found great differences in the behavior of the two gases, both in the rates of adsorption and in the amounts adsorbed. In the course of this work we have also determined, by direct measurement, the heats of adsorption of the two gases at 0°. An interesting by-product of the work has arisen from a detailed study of the rates of adsorption at −78° on a comparatively bare copper surface. Under these conditions it has been found that the adsorption process is autocatalytic.

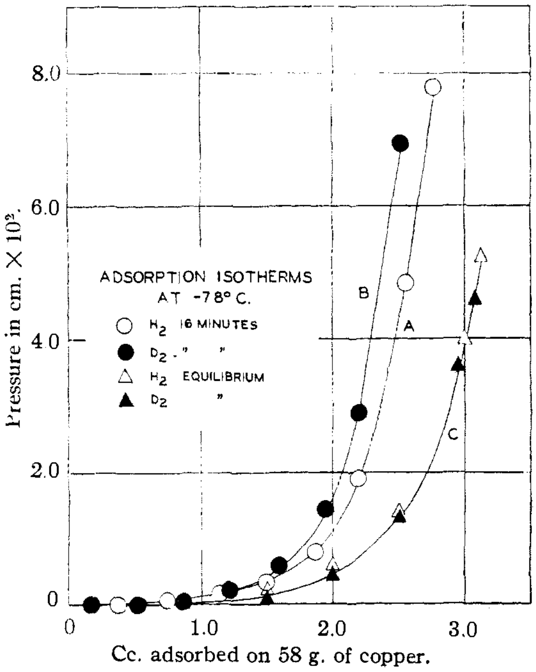

Fig. 1.

Experimental Details

Apparatus.—The general apparatus assembly and experimental procedure were in most details identical with those previously used by Beebe.[6] In the heat measurements smoother time–temperature curves were obtained by protecting strained portions of the constantan thermocouple wire from chance changes in room temperature. Moreover the sensitivity of the thermometric system was approximately tripled by use of a more sensitive galvanometer and a longer optical arm. The velocity of adsorption was measured on a McLeod gage by observing the rate of decrease of pressure in the system after admission of gas.

Materials.—Copper No. 1, used in most of the experiments, was prepared by reduction of high grade copper oxide granules in a stream of pure, dry hydrogen first at 120 and finally at 170°. After each series of adsorption measurements, the catalyst was degassed at 170° by use of a mercury diffusion pump over a period of five to fifteen hours. The copper, protected from mercury vapor by a trap containing cadmium turnings and gold foil, maintained a constant adsorptive capacity after several months of use. Copper No. 2 was prepared in exactly the same manner as No. 1, but a different sample of copper oxide was used. Copper samples No. 1 and 2 had approximately equal adsorptive capacity.

Copper No. 3, a much less active sample than the others, was prepared from copper powder made by rapid deposition from a solution of copper sulfate at high current density. This powder, supplied through the courtesy of Dr. F. H. Willard, was reduced in the same manner as were the others to remove surface oxide.

Electrolytic tank hydrogen was purified by passing it over copper at 450°, solid potassium hydroxide, and anhydrous magnesium perchlorate in sequence.

The deuterium gas, kindly supplied by Professor H. S. Taylor, was made by electrolysis of 99% heavy water produced in the Princeton Laboratory of Chemistry. A part of the work reported in this paper was done with a sample of deuterium received in February, 1934. Because of the unexpected differences between the results obtained and those of Pace and Taylor on other adsorbents another sample was requested from Professor Taylor. This deuterium, received in September, 1934, yielded results entirely consistent with those from the earlier sample.

The source of helium, used to measure the dead space in the apparatus, has been described previously.[7]

Experimental Results

Comparison of Hydrogen and Deuterium.—That our experiments very definitely demonstrate differences in the adsorption of the two hydrogen isotopes will be seen from the data which follow. In Fig. 1 are shown the isotherms for hydrogen and deuterium at −78° on copper No. 1. Increments of gas were admitted at thirty-minute intervals. Curves A and B are plotted from data taken sixteen minutes after admission of each increment of gas. That the difference in the isotherms A and B is due entirely to a difference in the rates of adsorption is shown by curve C. Each point on this curve represents data taken after the pressure had remained constant for twelve hours or more indicating that equilibrium had been reached. The coincidence of the data for hydrogen and deuterium on curve C indicates that, at equilibrium, the two gases are adsorbed in equal amounts at −78° although their rates of

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(6) Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932).

(7) Beebe and Wildner, This Journal, **56**, 642 (1934).

adsorption differ, the rate for deuterium being slower. These conclusions were confirmed by direct rate measurements.

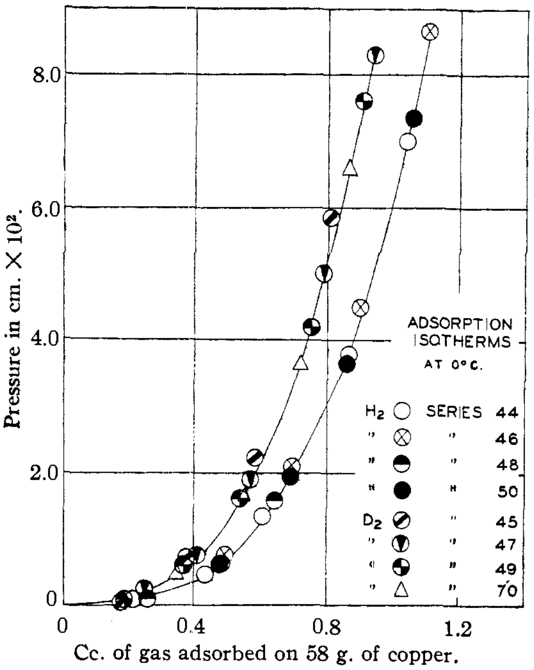

Fig. 2.

At 0° and higher temperatures the nature of the adsorption phenomena appears to be more complex than at −78°. It seems probable that a single type of sorption occurs at −78°, but that two types occur at the higher temperatures.[8] In obtaining the data at 0° for the isotherms shown in Fig. 2, increments were admitted to the catalyst at fifteen-minute intervals and readings were taken five minutes after each admission. That the isotherms do not represent equilibrium conditions is shown in Fig. 3, curve A. Ninety-two per cent. of the hydrogen admitted was adsorbed after five minutes, yet adsorption proceeded at a slow rate so that 2% more of the gas initially admitted had disappeared after six hours. Curve B shows similar results for deuterium. At first it seemed probable that the difference in the isotherms at 0° was due only to a difference in the rates of adsorption of hydrogen and deuterium, as was true at −78°. However, comparison of curves A and B in Fig. 3 reveals that there was still a definite difference in the amount of gas adsorbed under identical conditions even after six hours. In fact the two rate curves remained parallel at the end of five days although both hydrogen and deuterium were being adsorbed very slowly even then. As a further check of this apparent greater adsorption of hydrogen than of deuterium, rate measurements were repeated on copper No. 3. The results, which are entirely consistent with those of copper No. 1 at 0°, are shown in Fig. 4, (two curves at top).

Investigation of the adsorption process in the temperature range 0 to 125° revealed a rather surprising temperature inversion in the ratio of the amounts of the two isotopes adsorbed under identical conditions. The data measured on copper No. 3 are shown in Fig. 4. In all experiments 0.74 cc. of gas was admitted to a previously degassed sample weighing 45 g. which had been brought to the desired temperature. Experiments not shown were also performed at 19 and 125°. These yielded results which were entirely consistent with those which are shown for 0, 56 and 100°. The order of experiments was H_2 at 0°, D_2 at 0°, H_2 at 0°, H_2 at 19°, D_2 at 19°, H_2 at 56° D_2 at 56°, D_2 at 100°, H_2 at 100°, H_2 at 125°, D_2 at 125°, D_2 at 0°, H_2 at 0°.

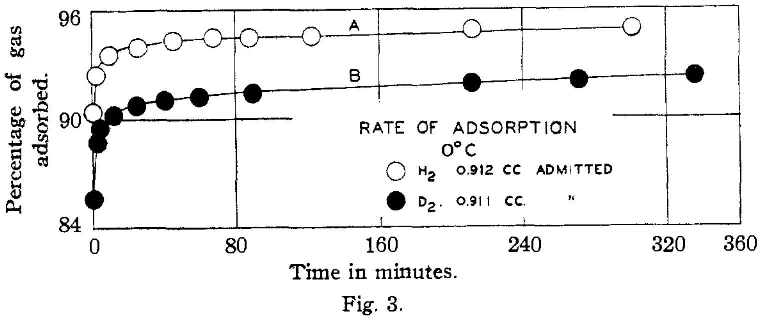

Fig. 3.

It is important to observe that the points at 0° indicated by triangles were obtained at the end of the series of experiments, whereas those represented by circles were obtained at the beginning of the series. It is therefore demonstrated that no change had occurred in the copper surface during the whole series. Moreover, it seems improbable that any effects due to exchange reaction could have been present. Otherwise one would not expect identical results for the initial experiment for deuterium at 0° (Fig. 4) conducted after a hydrogen experiment at 0°, and the final experiment for deuterium at 0° conducted after a deuterium experiment at 125°. The tempera-

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[8] Ward, *Proc. Roy. Soc.* (London), **A133**, 506 (1931).

ture inversion was also observed on copper No. 2 in experiments at 0 and 100°.

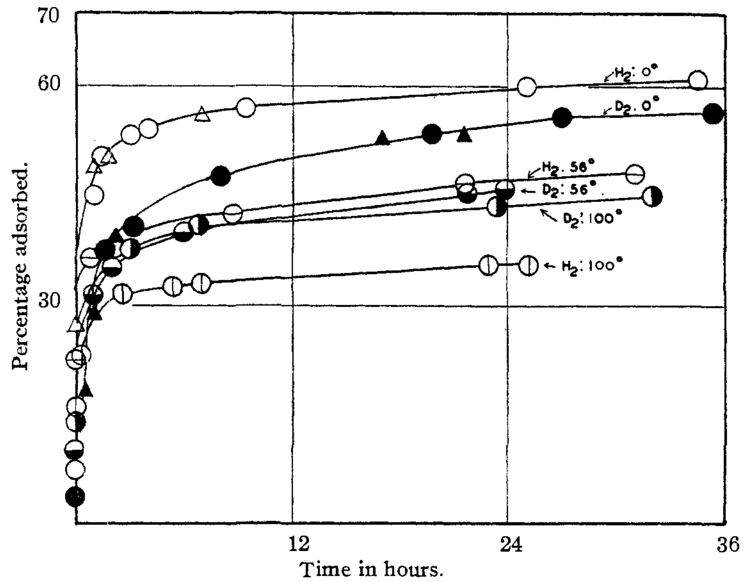

Fig. 4.—○ and ●: initial experiments; △ and ▲: final experiments.

Rates of Adsorption for Initial Stages.—A detailed study at −78° of the rates of adsorption of the two gases in the initial stages upon a comparatively bare copper surface revealed the surprising fact that the rate *increased* with increasing amounts of adsorbed gas on the surface. In other words, the process was autocatalytic. This point is best understood from Table I. A typical experiment (expt. 3 for H_2) will be described. To a newly degassed surface of copper No. 1, was admitted 0.387 cc. (increment 1); after four minutes 0.298 cc., or 77%, had been adsorbed, and after thirty minutes the whole 0.387 cc. was adsorbed. At this point increment 2, approximately equal in volume to 1, was admitted; after four minutes 97% was adsorbed, and after thirty minutes 100%. Increment 3 now followed and was 97.6% adsorbed after four minutes and 100% adsorbed after thirty minutes.

Examination of the data in Table I shows that deuterium exhibits the same unexpected rate phenomenon. The difference in rate between the first and second increments is even more marked than in the case of hydrogen. More details are to be seen in Fig. 5 showing the percentages adsorbed at two, four, six and eight minutes for experiments 3 and 4. It is also obvious from Fig. 5 that the velocity of adsorption on the comparatively bare surface at −78° is definitely less for the heavier isotope.

TABLE I

RATES OF ADSORPTION OF H_2 AND D_2 ON COPPER (58 G.) AT −78°

Expt.	Gas adsorbed	Cc. added	% adsorbed at 4 min.
3	H_2	0.387	77.0
		.369	97.0
		.383	97.6
7	H_2	.376	77.1
		.375	98.1
		.399	98.5
5	H_2	.170	94.2
		.170	99.4
		.174	100.0
4	D_2	.392	57.2
		.378	95.2
		.371	96.2
8	D_2	.387	53.5
		.394	95.0
		.366	96.0
9[a]	D_2	.381	46.5
		.393	95.2
		.387	96.2
6	D_2	.166	66.2
		.179	92.2
		.164	98.2

[a] Experiment 9 was made after another D_2 experiment, Expts. 4, 8 and 6 were made after H_2 experiments.

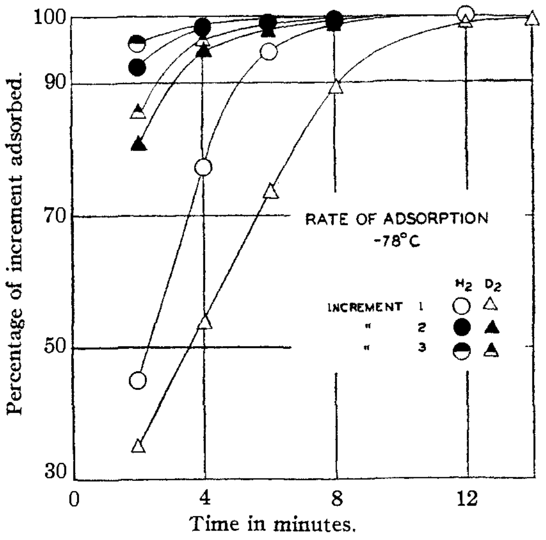

Fig. 5.

Owing to the rather striking results shown in Fig. 5 and in Table I, the authors have made a critical examination of the experimental procedure to see if the data could in any way be traced to experimental error. No such source of error was found. The obvious objection that the abnormal results could arise because the copper might not have cooled to −78° at the beginning of each experiment is eliminated because the catalyst tube was always left immersed in the bath at −78° overnight before each experiment. That this was sufficient time for thermal equilibrium was shown by the thermo-element which was used in the heat measurements.

Heats of Adsorption.—Altogether six series of measurements of differential heats of adsorption were made for hydrogen and five series for deuterium on two different samples of copper No. 1 weighing 67 and 58 g., respectively. Typical data are shown in Table II. The heats of adsorption are approximately 11,000 calories per mole of gas. No measurable difference was detected for the two gases. This observation is consistent with a calculated difference of 200 calories per mole, based on the values of the zero point energies of the H_2 and D_2 molecules and of the Cu–H and Cu–D bindings given by Eyring and Sherman.[9] The differential heats of adsorption for both isotopes decreased slightly with increasing amounts of gas already adsorbed. This decrease was not so marked, however, as was the case previously reported[10] for carbon monoxide on copper.

TABLE II

SERIES 23, ADSORPTION OF H_2 ON COPPER AT 0°

Increment	Volume of gas, cc. admitted	Volume of gas, cc. adsorbed	Residual pressure, mm. × 10^3	Differential heat of adsorption kcal. per mole
1	0.144	0.144	1.9	11.4
2	.138	.137	5.9	11.7
3	.186	.183	20.5	11.2
4	.163	.158	42	11.3
5	.161	.154	75	10.4
6	.162	.152	121	10.7
7	.207	.192	163	10.5
8	.322	.279	374	10.4
Total	1.483	1.399		
Series 25, adsorption of D_2 on copper at 0°				
1	0.230	0.230	16.6	12.4
2	.196	.191	41	11.8
3	.205	.194	88	11.3
4	.278	.252	202	11.1
5	.248	.208	375	11.5
6	.364	.293	778	10.5
Total	1.521	1.368		

Discussion of Results

Difference in Behavior of Hydrogen and Deuterium.—Our results like those of Klar and of Fajans previously cited appear to be in disagreement with the work of Pace and Taylor.[2] However, it should be mentioned that all of our measurements were carried out at low pressures (0 to 2 mm.), whereas those of Pace and Taylor were at 760 mm. It therefore seems possible that measurements on Pace and Taylor's active adsorbents at low pressure may very well uncover differences between hydrogen and deuterium which have been masked at 760 mm. On the basis of their observations Pace and Taylor have drawn certain conclusions concerning the probable rate determining factors in the adsorption process. Because of the apparent disagreement mentioned above, these conclusions should be reserved pending further experimental work.

Special attention is called to the similarity between our results and the data of Klar[4] on the relative rates of hydrogenation of ethylene over iron catalyst by the two hydrogen isotopes. The latter author reports that although the hydrogenation rate is greater for hydrogen than for deuterium at 0°, the reverse is true at temperatures above 100°; and suggests as a tentative explanation the possibility of a temperature inversion in the ratio H_2/D_2 adsorbed entirely analogous to that directly observed by us in the case of copper. Pease and Wheeler[11] recently have reported preliminary data on the rates of hydrogenation of ethylene over copper catalyst. They have found for the ratio of rates H_2/D_2 a value of 1.59 at 0°, 1.34 at 184° and 1.04 at 306°. They suggest the possibility that their results may be accountable to an exchange reaction absent at 0°, but increasingly present at higher temperatures. It seems possible to us that an explanation similar to that offered by Klar in the case of iron catalyst may be applied to Pease and Wheeler's results. Our data show that deuterium is relatively more strongly adsorbed with increasing temperature as compared to hydrogen. It may be that the higher energy of activation for the deuterium reaction causing a slower rate of hydrogenation of ethylene at 0°, is increasingly compensated with rising temperature by the relatively greater adsorption of deuterium as compared to hydrogen.

It is difficult at this time to attain a satisfactory theoretical explanation of the complex

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(9) Eyring and Sherman, *J. Chem. Phys.*, **1**, 348 (1933).

(10) Beebe and Wildner, THIS JOURNAL, **56**, 642 (1934).

(11) Pease and Wheeler, *ibid.*, **57**, 1144 (1935).

differences in the adsorption data for the two gases. All of our data on rates of reaction were obtained by measuring change of pressure with time. Because changes in pressure effect changes in the activation energies of adsorption processes,[12] no attempt has been made to calculate activation energies from the velocity curves. It is highly desirable to procure velocity data at constant pressure using a method for pressure control during the adsorption in the low pressure region (0 to 2 mm.).

Autocatalytic Adsorption at −78°.—One other example of autocatalytic adsorption has been observed previously by Benton and White[13] for hydrogen on iron at 0°. In these cases of autocatalytic adsorption the gas is apparently more readily adsorbed on those portions of the surface which are adjacent to atoms or molecules already adsorbed. There is little doubt that the adsorption of either hydrogen isotope on copper at −78°, which we have found to be autocatalytic, is of the activated type.[14] This possibility of an autocatalytic activated adsorption process presents a complicating factor which must be considered in connection with any adsorption theory of catalysis.

Summary

1. Very definite and complex differences have been found between the adsorptions of light and heavy hydrogen on active copper at low pressures (0 to 2 mm.).

2. At −78° the rate of adsorption is less for deuterium than for hydrogen, but equal amounts of the two isotopes are adsorbed at equilibrium.

3. In the temperature interval 0 to 125° the ratio H_2/D_2 adsorbed undergoes an inversion, hydrogen being more strongly adsorbed at the lower temperatures and less strongly at the higher temperatures.

4. The differential heats of adsorption have been measured by a direct calorimetric method, and are identical for the two isotopes within the limits of experimental error.

5. The early rate of adsorption of hydrogen at −78° is autocatalytic. The same is true for deuterium.

AMHERST, MASS. RECEIVED JUNE 28, 1935

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[12] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

[13] Benton and White, *ibid.*, **54**, 1820 (1932).

[14] At −78° the adsorption proceeded at a measurably slow rate and the residual pressure, even after the third increment of gas, was less than 10^{-3} cm. Both these observations together with evidence not detailed here, indicate activated adsorption. See also Benton and White, *ibid.*, **53**, 3304 (1931).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Coefficient of Expansion of Silver Iodide and of the Halides of Thallium

BY GRINNELL JONES AND FREDERIC C. JELEN

Introduction

Silver iodide has been reported to have a negative cubical coefficient of expansion. Since this property is almost unique it seemed desirable to test the reliability of the reports by a new experimental method and to measure the expansion of several analogous salts in the hope that another similar case might be found. In this paper data on silver iodide and the halide salts of thallium are reported.

The coefficient of expansion of silver iodide was determined many years ago by Fizeau,[1] and by Rodwell[2] with very discordant results, although both agree as to the negative sign.[3] Fizeau, using an optical interference method, obtained agreeing results on a cylinder which had been previously fused and therefore consisted of closely packed crystals and on precipitated silver iodide which was compressed into a cylinder. He found the cubical coefficient to be -4.1×10^{-6} at a mean temperature of 40°. A single large crystal gave -2.7×10^{-6}. Rodwell who measured the cubical coefficient by a dilatometer method obtained a much larger value, namely -55.7×10^{-6} between 21 and 67°. Klemm, Tilk and v. Müllenheim,[4] using a dilatometer method have found the cubic coefficient of expansion from 20 to 120° of thallous chloride to be 1.68×10^{-4}, and of thallous bromide to be 1.72×10^{-4}.

Outline of the Principle of the New Method.—Our method was suggested by the Richards[5]

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[1] H. Fizeau, *Pogg. Ann.*, **132**, 292 (1867).

[2] G. F. Rodwell, *Chem. News*, **31**, 5 (1875).

[3] Grinnell Jones, THIS JOURNAL, **31**, 191 (1909).

[4] W. Klemm, W. Tilk and S. v. Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 1 (1928).

[5] T. W. Richards and W. N. Stull, *Publ. Carnegie Inst. Wash.*, No. 7 and No. 76; T. W. Richards and Grinnell Jones, THIS JOURNAL, **31**, 158 (1909).