considered as evidence in favor of the relationship between entropy change and band shift.

As far as the hydrogen chloride data go, the proportionality between shift in wave length of the infrared absorption band of the solute and its change in entropy seems to be valid. It must be noted, however, that if this relationship is true its ·derivation has been somewhat fortuitous because of the limited accuracy of much of the solubility data employed. Relatively small deviations in the solubility determinations may lead to very large deviations in the thermodynamic quantities which depend on them. While additional and more accurate experimental work will be necessary to fully establish the validity and accuracy of this rule, as it now stands, applicable at least approximately to several hydrogen chloride solutions and in solvents of different types, it seems to be more than a coincidence, and may be of some value.

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Summary

1. Measurements are reported of the partial vapor pressure of hydrogen chloride from its solutions in benzene and in chlorobenzene at 30 and 40°, and in nitrobenzene at 20, 25, 30 and 40°. These include new measurements for nitrobenzene solutions at 25° and for benzene solutions at 30°.

2. These data together with those already in the literature were used to calculate the change in heat content and in entropy of the solute in the formation of these solutions.

3. A comparison of the derived thermodynamic data with infrared absorption data suggests a straight line relationship between the entropy change of the solute and the shift in its 3.46 μ vibrational band produced by the solvent.

Adsorption. I. The Effect of Heat Treatment on the Low Temperature Adsorption of Nitrogen by Aluminum Oxide

BY K. A. KRIEGER

In beginning an extended study of the adsorptive properties of aluminum oxide, it has seemed advisable to study first the effect of various methods of cleaning the adsorbent surface. This paper describes a study of the commonly used method where the adsorbent is simultaneously heated and evacuated. The effect of varying temperatures of evacuation upon the surface area and upon the average heat of adsorption of nitrogen in the first layer, as measured by the procedures of Brunauer, Emmett and co-workers,[1] has been ascertained.

Apparatus and Materials

The apparatus was similar to that of Durau[2] but mercury valves replaced all the stopcocks in contact with the gas under investigation except one graphite lubricated and mercury-sealed stopcock which served to isolate the adsorbent from the measuring system. An air thermostat enclosed the entire measuring system and was maintained at 30.00 ± 0.01° by a regulator of the Gouy type.[3] Temperatures were measured with a mercury thermometer calibrated against a Bureau of Standards resistance thermometer.

Pressures were measured with a steel scale and corrected for thermal expansion and for the value of g at Philadelphia. All readings were made with a cathetometer.

The liquid nitrogen used for cooling was not analyzed for purity, but any error thus introduced was eliminated by calibrating the empty apparatus with hydrogen and nitrogen, using several samples of liquid nitrogen. No variation in the properties of these samples was observed. The temperature of the liquid nitrogen was calculated from atmospheric pressure.[4]

High temperatures were measured and regulated by means of a Chromel–Alumel thermocouple calibrated against Bureau of Standards melting point standards, and a pyrometer controller. The temperature variation was approximately ±4°, and the absolute error about the same.

(1) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(2) Durau, Z. Physik, **101**, 27 (1936); see Fig. 3, p. 33.

(3) Sligh, THIS JOURNAL, **42**, 60 (1920). This almost forgotten device has proved exceedingly effective, diminishing the temperature variation of this thermostat to about one-tenth of that observed with the conventional, non-oscillating regulator.

(4) "International Critical Tables," Vol. III, p. 203.

The dead-space was determined at 30.00° with nitrogen in the usual way. No indication of adsorption of nitrogen at this temperature was obtained. The error in measurement of the dead-space, together with an error of ±0.1 mm. in pressure measurement, led to an estimated over-all error somewhat less than ±0.5%.

The sample of aluminum oxide used was Alorco Activated Alumina. It was a portion of a larger quantity reserved as a standard.

Compressed hydrogen was purified by passage through a hot copper tube, towers of calcium chloride and sodium hydroxide, and a liquid air trap; compressed nitrogen by passage through the last three.

Experimental Results

The experimental results are given in Table I, where p is the pressure in cm. of mercury, x is moles of nitrogen adsorbed per gram of aluminum oxide, and $p/[x(p_0 - p)]$ is Brunauer's function.[1] The temperature of adsorption was in every case 77.3°K., and the weight of the sample 1.352 g.[5] The adsorption was strictly reversible, and equilibrium, even at the highest pressures, was established within a few seconds.

TABLE I

p	$x \times 10^5$	$\dfrac{p}{x(p_0-p)}$	p	$x \times 10^5$	$\dfrac{p}{x(p_0-p)}$
		Run 1a, $p_0 = 76.30$			
0.01	48.4	0.27	5.90	180.5	46.4
.10	91.9	1.4	7.27	188.2	56.0
.60	126.2	6.3	8.39	195.8	63.1
.70	128.5	7.2	9.60	203.1	70.9
.79	131.6	7.9	10.92	209.6	79.7
1.58	144.9	14.6	12.22	216.5	88.1
2.05	150.1	18.4	13.69	224.1	97.6
4.10	169.4	33.5	15.06	232.5	105.8
		Run 1b, $p_0 = 75.80$			
12.80	224.5	90.5	18.51	256.3	126.1
14.66	234.9	102.1	20.62	270.5	138.1
16.62	246.0	114.1	22.63	283.6	150.1
		Run 2a, $p_0 = 74.80$			
4.42	177.1	35.5	19.01	265.1	128.5
5.63	186.2	43.7	21.22	277.3	142.8
6.60	192.3	50.3	23.61	292.9	157.5
7.66	199.0	57.4	25.99	307.2	173.4
14.67	239.9	101.6			
		Run 2b, $p_0 = 76.98$			
6.35	188.6	47.7	9.23	204.2	66.7
7.26	194.0	53.7	10.32	210.4	73.6
8.24	199.4	60.1	11.35	216.9	79.7
		Run 3a, $p_0 = 75.46$			
7.36	206.7	52.3	10.67	225.1	73.2
8.42	212.9	59.0	11.93	232.4	80.8
9.54	219.4	66.0	13.19	239.1	88.6
		Run 3b, $p_0 = 76.30$			
8.03	212.7	55.3	11.67	232.5	77.6
9.20	219.2	62.5	13.04	240.4	85.7
10.44	226.0	70.2	14.40	247.9	93.8
		Run 4a, $p_0 = 76.23$			
8.96	182.3	73.1	13.34	200.2	106.0
10.32	188.6	83.0	14.82	210.3	114.8
11.81	194.7	94.2	16.56	216.9	128.0
		Run 5a, $p_0 = 75.90$			
3.17	83.1	52.4	9.67	98.5	148.2
4.01	85.3	65.4	11.24	101.5	171.3
5.66	89.0	90.5	12.88	104.5	195.6
6.45	90.3	102.9	14.86	108.1	225.2
8.27	95.3	128.3	16.93	111.8	256.8
		Run 5b, $p_0 = 76.14$			
6.43	87.9	104.9	13.17	100.7	207.7
7.55	89.9	122.4	22.87	119.3	359.9
8.79	92.1	141.7	26.74	128.1	422.6
10.09	94.1	162.3	30.99	138.2	496.6
11.57	97.7	183.4	40.06	166.0	668.9

Summary

Run	x_m, millimoles/g.	$E_1 - E_2$, cal./mole	T	t
1a	2.01	607	210	25
1b	1.92	598	210	30
2a	2.07	618	318	11
2b	2.02	639	318	21
3a	2.10	657	528	18
3b	2.12	657	528	35
4a	1.76	699	734	35
5a	0.89	805	938	27
5b	.85	839	938	49

In the summary x_m is the quantity of nitrogen required to form a monomolecular layer of gas and is, therefore, a measure of the surface of the adsorbent; $E_1 - E_2$ represents the difference between the average heat of adsorption in the first layer and the heat of liquefaction of nitrogen at 77.3°K. These quantities were obtained from Brunauer's formula: $p/x(p_0 - p) = 1/x_m c + (c - 1)/x_m c \times p/p_0$, where $E_1 - E_2 = 2.303RT \log c$, by graphical extrapolation of $p/x(p_0 - p_0)$ vs. p/p_0, whence $c - 1/x_m c$ is the slope and $1/x_m c$ the intercept. The curves for Runs 1a, 4a and 5a are shown in Fig. 1. The others are omitted to avoid crowding. T is the temperature, in degrees C., and t the time, in hours, of preheating.

Discussion

Examination of the data in the summary shows that for temperatures of activation (preheating temperatures) not exceeding 528°, the surface area and $E_1 - E_2$ are sensibly constant at 2.04 millimoles/g. (±3%) and 629 cal./mole (±4%), respectively.[6] Further increase of the tempera-

(5) The sample was heated at 110° to constant weight. If such a sample be ignited at 800 to 1000° for one to two hours, a further loss in weight amounting to 8.4% will be observed.

(6) There is a distinct trend in the $E_1 - E_2$ values, but it is difficult to be sure that the trend is not fortuitous. The value of c, and therefore of $E_1 - E_2$, depends both upon the slope and intercept of the lines (Fig. 1), and since the intercept is small, a small error in extrapolation produces a large change in c. Fortunately, $E_1 - E_2$ varies with $\log c$, thus reducing the sensitivity of $E_1 - E_2$ to errors in ex-
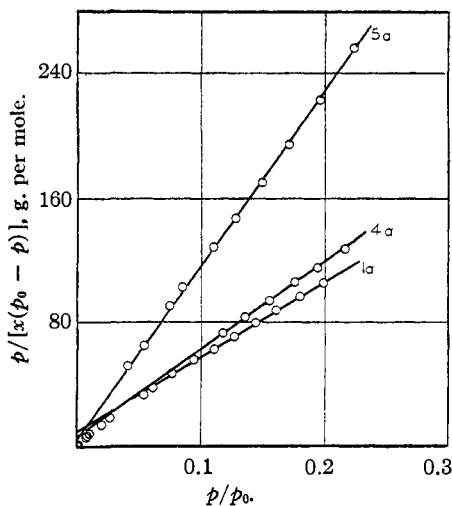
Fig. 1.

ture of activation of 734° (Run 4a) decreases the area by nearly 15% and increases $E_1 - E_2$ by about 10%. Finally, heating to 938° further reduces the area by 40% and increases $E_1 - E_2$ by 20%.[7] It is interesting to note in this connection that this last value of $E_1 - E_2$ is very close to that obtained by Brunauer for a wide variety of substances.

Although, in the writer's opinion, a definitive explanation of these phenomena must await the accumulation of further experimental data, it is perhaps in order to formulate the more obvious possibilities. The simplest hypothesis requires only the operation of some mechanism destructive to the adsorptive capacity of centers of lower energy of adsorption; since $E_1 - E_2$ is an *average* taken over the first adsorbed layer, the inactivation of centers of lower energy would, of course, increase the *average* energy while reducing the area. There is much evidence in the literature, however, which suggests that, at least for some adsorbents, an increase in temperature of activation produces a net increase in adsorptive capacity and, hence, presumably an increase in effective area. This apparent in-

crease[8] in area is probably due to the removal of substances already present on the surface, and not to the formation of new areas for adsorption. In the face of such observations, the possibility that two processes, removal of gases from centers of higher energies of adsorption and destruction of areas of lower energies, occur simultaneously must not be forgotten, and further work is in progress in the writer's laboratory in the hope of finding a means of distinguishing the two processes.

In one respect these findings appear contrary to the weight of catalytic experience, which teaches that the decrease of catalytic activity produced by excessive heating is due to the destruction of the centers of higher activity; but it must be remembered that in the present case the temperatures and heats of adsorption involved are not of the magnitudes expected in catalytic measurements, and there is no ground for the supposition that data from measurements in this region are transferable to regions of interest in catalysis. Moreover, some recent work[9] appears to imply that the catalytic centers which cause reaction to take place are not necessarily identical with those which hold the reacting molecules within the range of the forces that produce reaction; and if this suggestion should prove to be generally applicable, then destruction of the centers of lower activity would be sufficient to account for a decrease in catalytic activity.

Summary

1. The effect of preheating upon the surface area of a sample of aluminum oxide and upon the heat of adsorption of nitrogen on the surface has been measured.

2. Tentative explanations of the observed phenomena have been given.

trapolation. Pairs of runs made at the same temperature duplicate $E_1 - E_2$ values within about 3%, but this does not necessarily represent the maximum error.

(7) According to Ulrich, *Mineralog. Abstr.*, **3**, 21 (1926), aluminum oxide is converted to an isometric form by heating to 925°.

(8) Fajans, *Z. physik. Chem.*, **B28**, 252 (1935). For a general discussion of these phenomena see: Taylor, *Proc. Roy. Soc.* (London), **A108**, 105 (1925); *J. Phys. Chem.*, **30**, 145 (1926); also Schwab, Taylor and Spence, "Catalysis," D. Van Nostrand Co., New York, N. Y., 1937.

(9) Turkevich and Selwood, THIS JOURNAL, **63**, 1077 (1941)