

of the third law can be made which is less open to this objection. For this purpose it is necessary to recognize varying types of reactions in condensed systems, depending in any given case upon the number of specifications required to define the unit cells, in addition to the number of molecules, of each substance involved in the reaction. The statement of the third law which it is desired to propose then is: *At the absolute zero entropy changes in all reactions of the same type are equal, and in reactions in which the system does not change in type entropy changes are zero.*

### Summary

The argument is made that there is in the ideal case no sharp dividing line between the crystalline and the (supercooled) liquid states. If the conclusion of Lewis and Gibson is accepted that glasses possess finite entropy at the absolute zero, it is necessary to believe that complicated crystals also do. Following Lewis and Gibson, randomness is regarded as the source of the entropy differences among glasses and crystals at the absolute zero, and the minimum number of atomic positions necessary to define the state of any system is adopted as a measure of its randomness. From the results of certain plausible assumptions as to the form of the relation between entropy and randomness, it appears possible that measurable entropy effects may be found in real crystals of the more complex types. Finally, a statement of the third law is proposed which is in harmony with these ideas.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

## A RAPID METHOD FOR THE DETERMINATION OF HEATS OF ADSORPTION AND SOME VALUES FOR HYDROGEN ON NICKEL AND COPPER

BY RALPH ALONZO BEEBE AND HUGH STOTT TAYLOR

RECEIVED OCTOBER 19, 1923

In the course of investigations carried on in this Laboratory concerning the properties of metallic catalysts, it became desirable to obtain values for the heats of adsorption of various gases on those bodies. The case of hydrogen on nickel<sup>1</sup> was of particular interest and importance. A perusal of the literature revealed few of the data desired.

The first quantitative work of this kind was done by Favre,<sup>2</sup> although the thermal effect of adsorption had been observed by Mitscherlich<sup>3</sup> in his very excellent paper "Sur L'affinité Chimique." Favre, using a mercury calorimeter, obtained values for

<sup>1</sup> Gauger and Taylor, *THIS JOURNAL*, **45**, 920 (1923).

<sup>2</sup> Favre, *Ann. chim. phys.*, [5] **1**, 209 (1874).

<sup>3</sup> Mitscherlich, *ibid.*, [3] **7**, 18 (1843).

several gases on charcoal and for hydrogen on platinum. Chappuis<sup>4</sup> measured the thermal effect of several gases including sulfur dioxide, ammonia, and carbon dioxide on charcoal and meerschau, while Dewar<sup>5</sup> worked on heats of adsorption of the permanent gases on charcoal at liquid-air temperature making use of his liquid-air calorimeter. Titoff<sup>6</sup> with the aid of a Bunsen ice calorimeter obtained consistent values for the thermal effect of adsorption of nitrogen, ammonia, and carbon dioxide on charcoal as did Lamb and Coolidge<sup>7</sup> for organic vapors on the same adsorbent. Practically the only dependable quantitative work for metals is that of Ramsay, Shields and Mond<sup>8</sup> for hydrogen on platinum, since the earlier values of Favre were vitiated by the fact that he was not using a clean platinum surface.

In entering the field the authors desired to obtain measurements for heats of adsorption for numerous combinations of metals and gases. Hence it was decided to develop a more facile if somewhat less accurate method than that of ice calorimetry.

**Apparatus.**—In principle the apparatus was simple, the catalyst tube itself serving as the calorimeter.

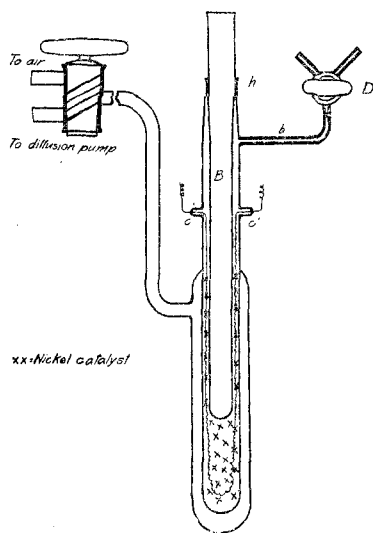


Fig. 1

The metal catalyst was contained in the inner chamber of a Dewar vessel, Fig. 1, which could be evacuated through the capillary tube *b* and the 3-way stopcock *D* by means of a Töpler pump. The outer chamber of the vessel was connected to a mercury diffusion pump and could be evacuated within a period of ten minutes to a pressure of  $10^{-5}$  mm. as read on the McLeod gage. The tube *B* reaching to the center of the catalyst mass carried a Beckmann thermometer. The joint at *h* was made vacuum tight with De Khotinsky cement. A platinum-iridium resistance wire of 8 ohms' resistance, insulated from the metal by thin-walled glass tubing to prevent short circuiting, was distributed as evenly as possible throughout the catalyst mass.

The resistance wire was connected to a voltmeter, ammeter, and 2-volt storage battery system by means of stout platinum leads which were fused through lead glass at *c* and *c'*. For measurements at partial pressures a manometer was connected to the catalyst bulb. The gases were collected and measured in the gas buret and leveling device described by Pease,<sup>9</sup> and were admitted to the catalyst bulb through the stopcock *D*.

**Calibration for Heat Capacity.**—The system was calibrated electrically by means of the platinum-iridium resistance wire, and the thermal capacity in calories was obtained from the equation: calories = (volts  $\times$  amperes  $\times$

<sup>4</sup> Chappuis, *Wied. Ann.*, **19**, 21 (1883).

<sup>5</sup> Dewar, *Proc. Roy. Soc.*, **74**, 122, 127 (1904).

<sup>6</sup> Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

<sup>7</sup> Lamb and Coolidge, *THIS JOURNAL*, **42**, 1146 (1920).

<sup>8</sup> Ramsay, Shields and Mond, *Z. physik. Chem.*, **25**, 657 (1898).

<sup>9</sup> Pease, *THIS JOURNAL*, **45**, 1196 (1923).

seconds  $\times 0.2392$ )/temperature rise in degrees. An ice-bath was placed about the tube up to the point B, care being taken to cover the platinum lead wires at c and c'. It was found that these lead wires conducted heat into the system in amounts which varied with room temperature if they were allowed to protrude into the air above the ice. In order to have the conditions the same for the calibration as for the actual heat of absorption measurement the catalyst bulb was filled with an atmosphere of hydrogen. The Beckmann thermometer was placed in its position, the outer jacket evacuated to  $10^{-5}$  mm. pressure, and when the system had reached thermal equilibrium with the ice-bath, it was ready for the calibration measurement. The platinum leads were connected through mercury cups by stout copper wire to a d. c. voltmeter and through another circuit to a d. c. 2-volt

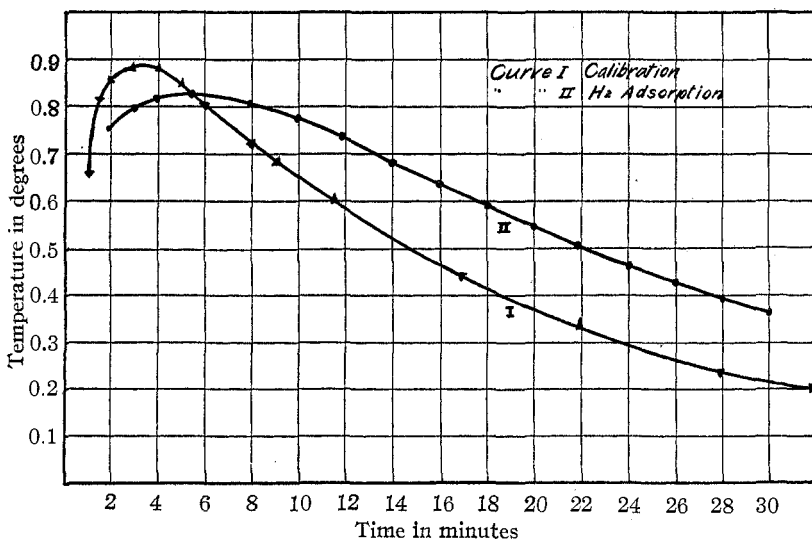


Fig. 2

storage battery with a double-throw switch and d. c. ammeter in series. Since the resistance of the stout platinum lead wires was negligible as compared to that of the fine platinum-iridium resistance wire, it was assumed that the total drop in potential and hence the total thermal effect occurred within the catalyst mass. By means of the double-throw switch the current was passed for some time through an outside resistance just equal to that of the resistance wire inside the calorimeter until the reading on the ammeter had become constant. In this way a steady state was assured during the time the calorimeter was to be heated by the electric current. The current was now passed through the resistance wire for a period of time which was read to a tenth of a second on a stop watch. The readings of the current flow on the ammeter and of the potential difference across the

terminals at  $c$  and  $c'$  as read on the voltmeter, were recorded. Thermometer readings at one-minute intervals were recorded until the temperature of the system, after the initial rise, had fallen back approximately to equilibrium temperature. As is obvious from Curve I, Fig. 2, a correction must be made for the cooling effect in the first two or three minutes up to the time when the maximum temperature has been attained. The amount of this correction was determined in the following manner. The system was heated to a temperature considerably above that used in the given calibration and the cooling curve was obtained from the time-temperature readings. The rate of cooling for any temperature gradient could now be determined by drawing the tangent to the curve at that temperature. Thus, the cooling correction for temperature gradients corresponding to the average temperatures for the first, second, third minutes, etc., were read directly from the cooling curve and were added to the apparent temperature rise to give the true value. By variations in the time of passing the current, the system was calibrated at different values of  $T-T_0$  ( $T$  being the maximum temperature, and  $T_0$  the equilibrium temperature) and these variations were found to have no effect on the values obtained. The accuracy of these calibrations was about 2%.

**Procedure for Measurement of Heat of Adsorption.**—In outline, the method pursued was as follows. The volume of hydrogen adsorbed was measured by the method of Taylor and Burns<sup>10</sup> using nitrogen as a reference gas and the concomitant thermal effect was measured on the thermometer. From the temperature rise and the volume adsorbed, since the heat capacity of the calorimeter was known, the molar heat of adsorption could be computed directly. One other factor had to be considered, however. This was the thermal effect accruing from (a) compression of the gas in entering the calorimeter, (b) cooling of the gas from room temperature to equilibrium temperature. The amount of this correction factor was evaluated by running blank determinations of thermal effect with nitrogen. Since nitrogen is not adsorbed<sup>11</sup> by nickel, any thermal effect observed when this gas was used was attributed to Effects a and b mentioned above. Since nitrogen and hydrogen are both diatomic gases, their heat capacities per unit volume are essentially the same. Hence it was assumed that the heating effects, a and b, would be the same for equal volumes of the two gases. Knowing the heat effect arising from the admission of 1 cc. of gas into the tube, it was possible to calculate the heat effect for hydrogen above

<sup>10</sup> Taylor and Burns, *THIS JOURNAL*, **43**, 1277 (1921).

<sup>11</sup> In addition to the fact that the values for nitrogen agree with those for helium on active nickel, the fact that nitrogen is not appreciably adsorbed was demonstrated by the following experiment. A nitrogen value was made with the calorimeter chamber filled with active nickel and another with the chamber filled with inert material, diatomic brick. The thermal effect was the same in the two cases. Unless the heat of adsorption were zero, this would indicate no adsorption of nitrogen by active nickel.

that of adsorption, taking into account the volume adsorbed as well as that necessary to occupy the free space of the system.

TABLE I  
TYPICAL DATA

Temperature of buret, 17.7°.			Pressure in buret, 769 mm.		
Time in minutes	Temp. rise ( $T - T_0$ ) °C.	Buret readings Cc.	Time in minutes	Temp. rise ( $T - T_0$ ) °C.	Buret readings Cc.
0	0	92.50	4	...	...
0.5	0.545	...	5	0.773	29.30
1	.655	...	5.5	.770	28.70
1.5	.715	...	6	...	...
1.5	.715	...	6.5	.755	28.23
2	...	30.70	7.5	.737	...
2.5	.762	...	7.5	.737	...
3	.772	...	9	...	27.20
3.5	.774	...	10	.683	...

At the end of five minutes:

Vol. hydrogen admitted <sup>12</sup> .....	60.80 cc.
Vol. nitrogen admitted to effect temperature equilibrium.....	2.19
Total hydrogen value.....	62.99
Nitrogen value (free space of catalyst chamber).....	47.27
Volume of hydrogen adsorbed.....	15.72
Apparent temperature rise.....	0.773°C.
Cooling correction (1st minute).....	.030
(2nd minute).....	.042
(3rd, 4th and 5th minutes).....	.135
True temperature rise.....	.980
Correction for temperature rise due to heat of compression and cooling of gas from room temperature to zero.....	.088
Temperature rise due to adsorption.....	.892
Heat capacity of calorimeter.....	11.20 cal.
Hence, heat of adsorption = $Q = \frac{11.20 \times 0.892 \times 22.400}{15.72}$	14.240 cal.

$Q = 14,240$  calories per gram molecule of hydrogen.

**A. Typical Adsorption Measurement.**—The catalyst chamber was evacuated at 300°, this temperature being maintained constant by an electrically heated air-bath. As soon as the system had cooled to room temperature the tube was surrounded by an ice-bath as in the calibration experiment, and the thermometer placed in its tube B. It was found that the time required for the system to reach equilibrium with the ice-bath temperature could be greatly shortened by (a) admitting air to the outer chamber of the Dewar vessel, and (b) admitting a measured volume of nitrogen to the inner catalyst tube. When these precautions were observed equilibrium was reached in about 100 minutes, whereas otherwise a period of several hours was necessary. The addition of nitrogen to the inner tube was especially imperative since the nickel, having been out-gassed at 300°, and then cooled to 0°, behaved as does charcoal cooled in liquid air.

<sup>12</sup> All volumes are reduced to 0° and 760 mm.

and its presence in the vacuum precluded the possibility of the existence of hydrogen in the gaseous state even at extremely low partial pressure. Since the extent of hydrogen adsorption by nickel at  $0^{\circ}$  is practically independent of the pressure<sup>1</sup> above 40 mm., the diminution of the partial pressure of hydrogen due to the presence of a few cubic centimeters of nitrogen would have no effect upon the hydrogen adsorption. As soon as the temperature became constant, the outer chamber was evacuated. In this case a sufficiently good vacuum could be maintained by having the diffusion pump in communication with the Dewar flask throughout the experiment. In this way any gas molecules were removed from the vessel as rapidly as they were desorbed from the walls. The hydrogen was now admitted to the catalyst chamber and both the thermometer and the hydrogen measuring buret were read at one-minute intervals. Since there was an appreciable drift in the adsorption of hydrogen by the nickel, the time required before the thermometer readings had attained a maximum and had begun to fall off again was considerably longer than in the case of the calibration, and as a result the correction for cooling was correspondingly greater. The rate of cooling for a given temperature gradient was determined from the calibration cooling curve and not from the curve obtained in the case of hydrogen adsorption since the latter was distinctly flatter due to the fact that small amounts of hydrogen were still being adsorbed and were liberating heat in the process. Thus, after the temperature had begun to fall, the slope of the tangent at any given point would indicate too low a value for the true rate of cooling. This point is clarified graphically in Fig. 2. It is obvious that Curve I is steeper than Curve II.

The preceding data and calculations for Ni-I, H<sub>2</sub>-III are given as typical.

**Discussion of the Method. A. Rapidity.**—The point which must be emphasized about this method for measuring heats of adsorption is the rapidity with which values may be obtained. Once the heat capacity and nitrogen values have been determined it has been found possible to make a complete determination in five hours including the time required for evacuation and subsequent cooling. Obviously, for any given sample of catalyst the heat capacity and nitrogen value may be determined once for all, and any number of measurements for the same or for different gases may then be made.

**B. Accuracy.**—We do not claim accuracy better than 10%, although for the same catalyst samples, under like conditions, the deviation from the mean is much less than this. In so far as the theoretical value of the results goes, a greater accuracy is not essential. The question arose whether changes in room temperature might not materially affect the values obtained. A brief calculation demonstrates that this affect is well within the experimental error. The maximum variation in room temperature during these experiments was  $10^{\circ}$ . Now, since the molecular heat capacity of hydrogen is about 6.5 cal., the heat liberated by one gram molecule in cooling  $10^{\circ}$  would be 65 calories. Hence, the maximum variation due to room temperature is  $65 \div 13,000 = 0.5\%$ . This, of course, may be corrected for in any given experiment.

**Preparation of Nickel Catalysts.**—Nickel samples 1 and 2 were prepared in the manner described by Gauger and Taylor, reduction being carried out at  $300^{\circ}$ . Although the two samples were prepared as nearly

as possible under the same conditions, Nickel 2 exhibits an adsorptive capacity double that of Nickel 1, in fact nearly 100% in excess of any values heretofore obtained in this Laboratory. This case admirably illustrates the fact that catalysts are not easily reproducible. It happened that Nickel 2 was a fine fluffy powder after reduction, whereas Nickel 1 was more granular in appearance. The difference in adsorptive capacity was probably due merely to difference in surface areas of the two samples.

**Results.**—The thermal effect,  $Q$ , in the adsorption of hydrogen has been quantitatively determined for two different samples of nickel. Nickel 1 weighed 28.5 g. and adsorbed approximately 17 cc. of hydrogen. After three values of  $Q$  had been determined, the catalyst was heated at 450° for 21 hours. At the end of this time the adsorptive capacity was 7 cc. of hydrogen.  $Q$  was determined for the nickel in this state of activity. The metal had lost its jet-black gloss, had turned to a dull gray and a considerable volume shrinkage was observed. Nickel 2, which weighed 26.4 g., adsorbed 35 cc. of hydrogen. This catalyst was also subjected to heat treatment until its adsorptive capacity for hydrogen was reduced to 16 cc. In the case of Nickel 2, however, values of  $Q$  at partial pressures of hydrogen were determined before the catalyst was de-activated by heat treatment. The results obtained are tabulated below. Table I shows that the values of  $a$ , the volumes adsorbed, do not check exactly for the same catalyst sample, because the rate of adsorption varied somewhat in different runs and hence the volumes adsorbed at the end of five minutes were not in exact agreement. This difference in rate of adsorption was probably due to a difference in cleanliness of the metal surface, the rate of adsorption being greater for a clean surface. Harned<sup>18</sup> noticed this same phenomenon in the case of adsorption of chloropicrin by charcoal.

TABLE II  
INTEGRAL VALUES OF HEAT OF ADSORPTION OF HYDROGEN ON NICKELS 1 AND 2

Sample	Deter- mination	$a$ Cc. (0—760) adsorbed by sample	$T-T_0$ True rise in temp.	$Q$ Heat of adsorption in calories per mole
1 (before heat treatment)	1	17.66	1.044°	14,500
	2	16.21	0.916	14,210
	3	15.72	0.899	14,240
1 (heated 21 hrs. at 450°)	4	7.86	0.636	20,300
	5	8.31	0.696	21,000
2 (before heat treatment)	1	34.36	1.951	13,350
	2	35.35	2.060	13,700
2 (heated 4 hrs. at 450°)	3	16.64	1.107	15,640
	4	15.81	1.065	15,350

From the so-called saturation pressures obtained in the adsorption isotherms for hydrogen on nickel, Gauger and Taylor<sup>1</sup> have calculated the

<sup>18</sup> Harned, THIS JOURNAL, 42, 372 (1920).

molecular heat of adsorption to be 2,500 calories. Rideal<sup>14</sup> from quite different theoretical considerations, obtained a value of 12,000 calories. Our experimentally determined values are more closely in agreement with

TABLE III  
DIFFERENTIAL VALUES FOR NICKEL 2 ( $Q$  AT PARTIAL PRESSURES)

Determination	Initial pressure in mm. mercury	Final pressure in mm. mercury	$a$	$T - T_0$	$Q$
3A	0	2.0	16.22	0.917	13,300
3B	2	760.0	16.23	.994	14,400
4A	0	1.9	7.52	.432	13,510
4B	1.9	8.2	8.69	.501	13,560
4C	8.2	654.7	14.75	.938	14,950
5A	0	2.7	10.64	.600	13,260
5B	2.7	8.7	12.20	.654	12,600
5C	8.7	703.4	6.82	.424	14,600

Rideal's value. Moreover, we find<sup>15</sup> that the pressures  $p_2$  and  $p_1$  in the integrated form of the Clapeyron equation,

$$Q = 1.99 \times 2.303 \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1} \quad (1)$$

should be those pressures at which equal weights of gas are adsorbed at the two different temperatures. In other words, the value of  $Q$  must be calculated from the isosteres, not the isotherms. Unfortunately, the data available from Gauger and Taylor's isotherms do not lend themselves readily to such a calculation. An examination of Fig. 1 of their paper shows that the isotherms at 218° and 184° are the only ones from which even two points of an isostere are obtainable with any degree of accuracy. A calculation, according to the above method, making use of the best isostere obtainable from these two isotherms, yielded a value of some 13,000 calories, in good agreement with our experimentally determined results.

**Integral Heat of Adsorption.**—In the integral values for  $Q$ , given in Table II, two factors should be remarked: (a) The magnitude of  $Q$ ; (b) the variation of  $Q$  with the past history of the catalyst. The latent heat of vaporization of hydrogen at its boiling point is some 450 calories per mole. Since the heat of adsorption is not even of the same order of magnitude it is certain that the adsorption of hydrogen by nickel is not a condensation phenomenon. The values of  $Q$  obtained from Nickel 1 and Nickel 2 show that the heat of absorption is actually higher in the case of the metal of lower adsorptive capacity. If the catalyst of higher adsorptive capacity is the more active, as has been demonstrated in the case of copper for the hydrogenation of ethylene,<sup>9</sup> then from our results the more active catalyst has the lower heat of adsorption. This would point

<sup>14</sup> Rideal, *J. Chem. Soc.*, 121, 309 (1922).

<sup>15</sup> Freundlich, "Kapillarchemie," Leipzig, Akademische Verlagsgesellschaft, sec. ed., 1922, pp. 181-182.



to the formation of a less stable hydrogen-nickel complex in the case of the active catalyst. More data would be needed before this observation could be accepted without reserve.

**Differential Heats of Adsorption.**—Freundlich likens the integral heat of adsorption to heat of solution and differential heats of adsorption, values obtained by determining  $Q$  for fractions of the total amount adsorbed by making determinations at different partial pressures, to heats of dilution. The results of Titoff<sup>6</sup> for ammonia on charcoal show a marked diminution of the heat of adsorption for increasing partial pressures of the gas, as would be expected if the case parallels that of dilution. The values obtained by us for hydrogen on nickel are anomalous in this respect and point definitely to a specificity of the adsorption phenomenon. As is seen in Table III, the values remain practically constant with increased pressure, and even exhibit an increase as the pressure approaches atmospheric.

**Integral Value of  $Q$  for Hydrogen and Copper.**—*Preparation of catalyst.* A sample of extraordinary activity was prepared by the reduction of copper oxide granules in a current of pure, dry hydrogen, at 140–150°. Great care was taken that the temperature should not exceed 150°. When reduction was complete, the copper was of a dull, brick-red color. The sample of copper used weighed 35 g. and adsorbed approximately 15 cc. of hydrogen at 0°. The thermal capacity of the system was 12.26 calories.

In this case, it was possible to obtain much more concordant values than in the case of nickel, since practically no error due to adsorption drift was introduced during the determination. Adsorption was complete at the end of three minutes and, as a result, the cooling curves for hydrogen adsorption and for thermal calibration had the same slope for any temperature gradient.

As in the case of nickel, the value of  $Q$  found is higher than would be expected if it were assumed that the adsorption is a condensation phenomenon. It will be interesting, after measuring the differential values of  $Q$  for hydrogen on copper, to see whether there is a change in the thermal effect for different partial pressures of hydrogen. It will be recalled that there was no such change for hydrogen on nickel. We hope to obtain these data for a later publication. The data obtained for the integral heat of adsorption are recorded in Table IV.

TABLE IV  
INTEGRAL HEAT OF ADSORPTION OF HYDROGEN ON COPPER

Cc. adsorbed	$T_2 - T_1$ °C.	$Q$
15.35	0.538	9,620
15.24	.531	9,560
15.42	.539	9,590

The authors wish to express their indebtedness to Professor G. A. Hulett, with whom the suggestion originated for the measurement of heats of

adsorption by the method herein recorded. For kindly criticism and advice when in difficulties, we are likewise grateful.

### Summary

1. A rapid method for measuring heats of adsorption of gases on metallic catalysts is described.

2. The integral value for the heat of adsorption of hydrogen on nickel varies from 13,500 to 20,500 calories depending upon the past history of the adsorbent. Corresponding values for the same samples are in good agreement.

3. The magnitude of the value shows that the phenomenon is not one of condensation in this case.

4. The differential values do not decrease with increasing partial pressure. In this respect the case is anomalous.

5. With copper as adsorbent of hydrogen more nearly concordant results are obtainable. The magnitude of the heat of adsorption is in this case 9600 calories. The case is therefore parallel to that of nickel.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 35]

## THE FREE ENERGY OF ANTIMONY TRIOXIDE AND THE REDUCTION POTENTIAL OF ANTIMONY

BY REINHARDT SCHUHMAN<sup>1</sup>

RECEIVED OCTOBER 23, 1923

### Purpose of the Research

Little reliable information is available about the free energy of formation of any compound of antimony. Its molal electrode potential is also very uncertain: it is given as  $-0.1$  volt by Abegg, Auerbach and Luther,<sup>2</sup> this value being taken from the results obtained by Neumann<sup>3</sup> in 1894. Lewis and Randall<sup>4</sup> point out the lack of information about the free energies of the compounds of a number of non-metallic elements, and antimony is included in the list.

The object of the present investigation was to determine (1) the free energy of formation of antimony trioxide, and (2) the molal electrode potential of antimony. These quantities were determined by measuring the electromotive force of cells of the type:  $\text{Sb}(s) + \text{Sb}_2\text{O}_3(s), \text{HClO}_4$

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<sup>2</sup> Abegg, Auerbach and Luther, "Elektromotorische Kräfte, Ergänzungsheft," Wilhelm Knapp, Halle, 1915, p. 48.

<sup>3</sup> Neumann, *Z. physik. Chem.*, 14, 193 (1894).

<sup>4</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 466.