Summary

1. Commercial cuprous oxide is inactive, and precipitated cuprous oxide heated above 85° in drying is partially inactivated catalytically.

2. Cuprous oxide dried below 85° and immersed in furfural causes hydrogenation of furfural at temperatures between 130 and 230° at pressures between 100 and 1900 p. s. i.

3. The addition of calcium oxide increases the rate of hydrogenation of furfural at the temperatures and pressures studied.

4. The addition of the product produced by treating vanadium(V) oxide with glucose (called vanadium(IV) oxide in this paper), or the addition of chromium(III) oxide to the optimum mixture of cuprous oxide and calcium oxide further increased the rate of hydrogenation of furfural.

5. The optimum proportions are approximately $Cu_2O:V_2O_4:CaO::1.0:7.14:1.4$ or $Cu_2O:Cr_2O_3:CaO::10:5:10$.

6. The cuprous oxide catalysts are prepared by grinding together, at room temperatures, the separately prepared oxides.

7. Under similar conditions of temperature and pressure the most active cuprous oxide catalysts produce more rapid hydrogenation of furfural than equal masses of the most active copper chromium oxide catalysts.[12]

[12] A very recent article describes the preparation of a copper-chromium oxide catalyst, active at room temperature but requiring 4000 p. s. i. of hydrogen in its preparation: Adkins, Burgoyne and Schneider, THIS JOURNAL, **72**, 2626 (1950).

AMES, IOWA RECEIVED DECEMBER 3, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF COLLOID SCIENCE, CAMBRIDGE UNIVERSITY]

The Determination of Heats of Adsorption by the Brunauer–Emmett–Teller Single Isotherm Method

BY CHARLES KEMBALL[1] AND G. D. L. SCHREINER

Although the theoretical foundations of the Brunauer–Emmett–Teller equation[2] are open to question, it has a wide applicability and has proved invaluable for the determination of surface areas of adsorbents. The equation may be expressed as

$$\frac{x}{v(1-x)} = \frac{1}{v_m c} + \frac{(c-1)x}{v_m c} \tag{1}$$

v being the volume of gas adsorbed, x the relative pressure, v_m the volume of adsorbate to form a monolayer and the constant c is given by

$$c = \frac{a_1 b_2}{a_2 b_1} e^{(E_1 - E_L)/RT} \tag{2}$$

a_1, a_2, b_1 and b_2 are constants connected with the formation and evaporation of the first and higher layers of adsorbed molecules, E_1 is the heat of adsorption to the first layer and E_L the latent heat of vaporization of the adsorbate.

The object of this paper is to demonstrate the conditions under which the ratio $a_1b_2/a_2b_1 = M$ will be equal to unity and to show how great the variations of its value may be. Brunauer and his co-workers[2] believed that M would not differ greatly from unity and that it was possible to determine E_1 by the measurement of c from a single isotherm. Several authors have suggested alternative assumptions about the value of M. Cassie[3] suggested that the value was about one-fiftieth and this was confirmed by Beebe and his co-workers,[4] who compared the calorimetric heats of adsorption of nitrogen on different charcoals with the values of E_1 obtained from equation (2). On the other hand, Hill,[5] like Cassie, using a statistical method, showed that M should have a value between 5 and 10 for diatomic molecules, and, in a recent paper,[6] calculated values of M lying between 2 and 20 for hydrogen iodide and for benzene molecules adsorbed on graphite. Davis and de Witt,[7] working with butane on glass spheres at more than one temperature, obtained values of M between 0.7 and 1.2. The need for a clearer understanding of the constant M, upon the value of which the determination of the heat of adsorption from a single isotherm depends, is illustrated by the remark of Gregg and Jacobs[8] who maintain that the difference between calorimetric and isosteric heats of adsorption and the BET values of E_1 is too irregular to be explained unless M be assumed to "vary in an unpredictable manner from one case to another." Recent papers by Hill[6,9] throw considerable light on the nature of the constant M, which is expressed as a ratio of the partition functions of adsorbate molecules in the adsorbed and in the liquid state. The present paper approaches the problem from a consideration of the entropy of adsorption as determined from experimental data. It is possible to show quite simply under what conditions M will be unity and how great the variations from unity may be.

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[1] Department of Physical Chemistry, Cambridge University.

[2] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[3] A. B. D. Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[4] R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, THIS JOURNAL, **69**, 95 (1947).

[5] T. L. Hill, *J. Chem. Phys.*, **16**, 181 (1948).

[6] J. W. Drenan and T. L. Hill, *ibid.*, **17**, 775 (1949).

[7] R. T. Davis and T. W. de Witt, THIS JOURNAL, **70**, 1135 (1948).

[8] S. J. Gregg and J. Jacobs, *Trans. Faraday Soc.*, **44**, 574 (1948).

[9] T. L. Hill, *J. Chem. Phys.*, **17**, 772 (1949).

Entropy of Adsorption and the BET Equation.—The standard state on the surface which will be used for consideration of the entropy of absorption will be defined by the bare fraction of the surface being equal to the fraction covered by one layer of molecules, or, in the BET terminology, $s_0 = s_1$. Objection may be raised that this standard state has no true thermodynamic significance and also relates to a region of the adsorption isotherm where the BET equation is known to fail experimentally. However, it is chosen deliberately because the derived differential thermodynamic functions are simply related to the BET constants c and M, and because it illustrates the physical significance associated with unit value of M. The standard state in the gas phase is taken as 1 atmosphere pressure and if $s_0 = s_1$ occurs at a pressure p', the partial molar or differential free energy change of the adsorbate on adsorption is given by

$$\Delta G_{\mathrm{A}} = RT \ln p' \qquad (3)$$

and it is related to the differential heat and the differential entropy of adsorption by the equation

$$\Delta G_{\mathrm{A}} = \Delta H_{\mathrm{A}} - T\Delta S_{\mathrm{A}} \qquad (4)$$

Using the equation given by Brunauer, Emmett and Teller[2] for the formation and evaporation of the first layer

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \text{ and } 1 = [(a_2 p_0)/b_2] e^{E_{\mathrm{L}}/RT} \qquad (5)$$

obtained from their equations (17) and (27), where p_0 is the saturation vapor pressure at the temperature T, we obtain

$$a_1 p s_0 = \frac{a_2 b_1}{b_2} p_0 s_1 e^{(E_{\mathrm{L}} - E_1)/RT} \qquad (6)$$

At the standard state, $s_0 = s_1$ (6) reduces to

$$p' = \frac{a_2 b_1}{a_1 b_2} p_0 e^{(E_{\mathrm{L}} - E_1)/RT} = p_0/c \qquad (7)$$

and using (3) the free energy is given by

$$\Delta G_{\mathrm{A}} = RT \ln p' = \\ - E_1 + T\left(E_{\mathrm{L}}/T + R \ln p + R \ln \frac{a_2 b_1}{a_1 b_2}\right) \qquad (8)$$

and, since the entropy of liquefaction of the adsorbate is given by

$$- \Delta S_{\mathrm{L}} = E_{\mathrm{L}}/T + R \ln p_0 \qquad (9)$$

(8) reduces to

$$\Delta G_{\mathrm{A}} = -E_1 - T\left(\Delta S_{\mathrm{L}} + R \ln \frac{a_1 b_2}{a_2 b_1}\right) \qquad (10)$$

Comparing (4) and (10) we have

$$\Delta H_{\mathrm{A}} = -E_1 \qquad (11)$$

and

$$\Delta S_{\mathrm{A}} = \Delta S_{\mathrm{L}} + R \ln \frac{a_1 b_2}{a_2 b_1} = \Delta S_{\mathrm{L}} + R \ln M \qquad (12)$$

From equations (10), (11) and (12) it is clear that M will be equal to unity only in those cases where the entropy of adsorption is equal to the entropy of liquefaction of the adsorbate. Alternatively if the free energy change is found from

$$\Delta G_{\mathrm{A}} = RT \ln p_0/c \qquad (13)$$

which is a combination of (3) and (7), and the value of E_1, determined by the single isotherm method on the assumption that $M = 1$, is used to give $-\Delta H_{\mathrm{A}}$, then the entropy change calculated from equation (4) will equal the entropy of liquefaction. This is illustrated by the three cases shown in Table I, where ΔG_{A} and ΔS_{A} are determined in this manner and ΔS_{L} is found from equation (9).

TABLE I

System	Temp., °K.	BET value of E_1 cal./mole	c	$-\Delta G_{\mathrm{A}}$ cal./mole	$-\Delta S_{\mathrm{A}}$ cal./deg.	$-\Delta S_{\mathrm{L}}$ mole	Ref.
CCl_4 on Al_2O_3	298	10,100	53	3470	22.2	22.2	8
N_2 on Grade 6 charcoal	77.6	2,180	132	753	18.4	18.4	4
EtI on unreduced iron	293	12,160	2110	5600	22.4	22.4	10

Discussion

In cases where the value of c is low and there is an appreciable number of molecules in the second and higher layers under the conditions defined by $s_0 = s_1$ the thermodynamic quantities will be slightly altered and it would be more nearly correct to write

$$\Delta H_{\mathrm{A}} = -E_1 + x$$

and

$$\Delta S_{\mathrm{A}} = \Delta S_{\mathrm{L}} + R \ln M - x/T$$

but this consideration does not alter the conclusion of the last section.

Since it is only in rare cases where the entropy of adsorption to the standard state $s_0 = s_1$, is equal to the entropy of liquefaction that M is unity, it is of interest to consider how greatly M may vary from case to case. The differential entropy change accompanying the adsorption of toluene on mercury[11] is large, being 50 cal./deg. mole or entropy units when the surface is half covered, whereas the entropy of liquefaction is 24 e.u. Equation (12) gives

$$R \ln M = -26 \text{ and hence } M = 2 \times 10^{-6}$$

An example showing a small change of differential entropy on adsorption is xenon adsorbed on mercury[12,13] where the figure is 14.2 e.u. compared with an entropy of liquefaction of 19 e.u. giving

$$R \ln M = 4.8 \text{ and } M = 11$$

These two examples show that M may vary over several orders of magnitude, having small values when the entropy of adsorption is greater than the entropy of liquefaction and *vice versa.* Unless theoretical considerations can be used to estimate the entropy of adsorption, and hence the value of M, the single isotherm method of determining heats of adsorption cannot be applied.

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(11) C. Kemball and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A187**, 53 (1946).

(12) H. Cassel and W. Neugebauer, *J. Phys. Chem.*, **40**, 523 (1936).

(13) C. Kemball, "Advances in Catalysis," Vol. II, 1949 p. 240

In their paper Drenan and Hill[6] give two calculated values for M in the case of hydrogen iodide adsorbed on graphite at 81.33° K. M is equal to 16.99 if the adsorption is non-localized and 2.16 if it is localized. As both these values are greater than unity the entropy of adsorption to the standard $s_0 = s_1$ must be less than the entropy of liquefaction which is an interesting and unexpected result, especially in the case of localized adsorption.

Summary

Equations are derived showing that the BET constant a_1b_2/a_2b_1 is unity only when the differential entropy of adsorption to a standard state on the surface defined by $s_0 = s_1$ (the bare fraction of the surface being equal to the fraction covered by one layer of molecules) is equal to the entropy of liquefaction of the adsorbate. It is also shown from published results that the value of a_1b_2/a_2b_1 may range at least from 10^{-5} to 10, and that the single isotherm method of determining heats of adsorption can only be used when the entropy of adsorption is known.

Cambridge, England Received May 8, 1950

[Contribution from the School of Chemistry of Rutgers University]

A Spectrophotometric Study of the Hydrolysis Products, Some Possible Complexes and Metal Salts of Fluoroboric Acid[1]

By Edward R. Scheffer[2] and Ellwood M. Hammaker

In the course of an investigation of fluoroboric acid, spectrophotometric analysis was studied as a possible method of identification and analysis of the acid, its hydrolysis products, and its compounds. An attempt was made also to determine the extent of complex formation, if any, of the fluoroborate ion and some of its hydroxy acids. In certain cases, the method of continuous variations as developed by Job[3] and improved by Vosburgh and Cooper[4] was applied in the study of possible complexes. The characteristic spectra of two hydrolysis products of fluoroboric acid have been obtained, and the general lack of any complexing tendency has been demonstrated.

Experimental

Measurements.—Light absorption measurements were made with a Beckman model DU spectrophotometer. Quartz or corex cells (1-cm.) were used, and all readings were made at room temperature.

Materials.—C. P. samples of hydrated cobalt and nickel nitrates were dissolved to give 0.1 M solutions (1) in water, (2) in 7.7 M hydrochloric acid and (3) in 42% aqueous fluoroboric acid. A 0.2 M solution of cupric sulfate was prepared from the C. P. hydrate. C. P. chromium metal was treated with 60% perchloric acid, 42% fluoroboric acid, and anhydrous $H[BF_2(OH)_2]$ to give solutions 0.03, 0.07 and 0.02 M, respectively, in chromium(III) ion. $H[BF_2(OH)_2]$ was prepared by the method of Sowa, *et al.*,[5] and $BF_3 \cdot 2H_2O$ was prepared by the method of Meerwein and Pannwitz.[6] Saturated aqueous solutions were prepared from technical sodium, potassium and ammonium fluoroborates. A 1 M solution of zinc fluoroborate was prepared from the pure hexahydrate. Technical lead fluoroborate solution (50.7%), purified tin(II) fluoroborate solution (47.7%) and cadmium fluoroborate solution (50.8%) were used as received.

The fluoroborate salts and solutions were very kindly furnished by the General Chemical Division, Allied Chemical and Dye Corporation.

Procedure and Results.—To investigate the possible formation of complexes between fluoroboric acid and cobalt(II) or nickel(II), respectively, three solutions were prepared for each ion as described under Materials. The nitrate salts were used in each case, because in dilute aqueous solutions the absorption is attributed to the hydrated ion and not to any complex formation with the nitrate ions. According to Job,[7] a 1 to 1 complex with the chloride ion is formed in hydrochloric acid of the concentration used. The absorption spectrum for each solution was determined, and the results obtained for cobalt are shown in Fig. 1. Similar results were obtained with nickel; in this case, however, the characteristic absorption maxima appeared at 720 and 395 mμ for the hydrated ion, and at 740 and 425 mμ for the chloride complex.

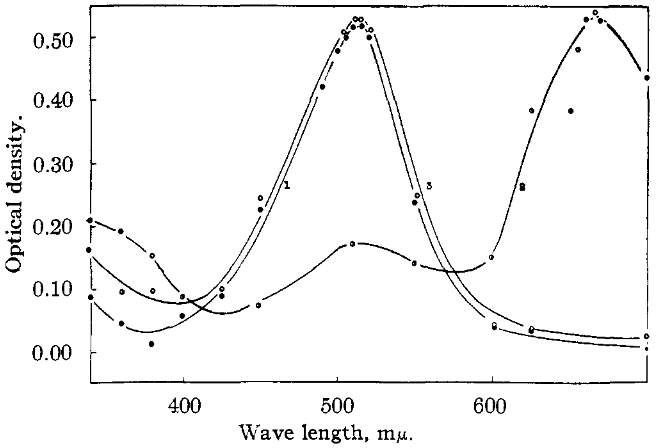

Fig. 1.—Absorption curves for cobalt(II) complexes: (1) aqueous solution, (2) hydrochloric acid solution, (3) fluoroboric acid solution.

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[1] Part of a thesis submitted by Edward R. Scheffer to Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] National Lead Company, Titanium Division, Sayreville, N. J.

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