3. Further studies of absorption spectra together with *p*H titration curves have made possible the postulation of structures for the two complexes. Titration curves indicate that the compound alkannin, which has not been studied spectrophotometrically, forms complexes analogous to those of naphthazarin.

4. Materials have been isolated, the compositions of which approximate those expected for the postulated structures.

Rochester, New York Received June 14, 1950

[Contribution from the Department of Chemistry, Iowa State College]

Cuprous Oxide as a Catalyst. I. Preparation and Promotion by Metallic Oxides[1]

By F. E. Brown, Ralph E. Menzel, Meredith M. Stewart and Philip A. Lefrancois

Few references to any catalytic action of cuprous oxide are found in the literature prior to 1937, and none of these references describe the treatment necessary to produce and retain the power to catalyze hydrogenations at moderate temperatures, 120 to 200°. Adkins and his collaborators[2,3] have described catalysts containing copper oxide and some of the other oxides which promote or stabilize or unite with copper oxide but these catalysts become inactive when the copper is reduced to the monovalent state.[4,5]

In 1937 Menzel[6] announced the discovery of the catalytic effect of cuprous oxide. Stewart[7] and Lefrancois[8] confirmed Menzel's discovery and extended the investigation of promoters.

General Procedure

The hydrogenation of furfural to form furfuryl alcohol was the reaction chosen for testing the catalysts. All experiments were conducted, batchwise, in one of the two electrically heated rocker type bombs described below. One, made in our shop, was copper lined and had a capacity of 3.85 l. In the experiments reported in this paper this bomb was charged with 3.00 moles of furfural. Calibration showed that when one mole of hydrogen reacted the pressure of the hydrogen decreased about 100 p. s. i., if the pressure was calculated to what it would be at 0°. The second was a commercial, unlined, chromium-nickel steel hydrogenation bomb. Its measured capacity was 0.495 l. It was charged with 0.50 mole of furfural and when one mole of hydrogen reacted the pressure decreased about 680 p. s. i. if pressures are reduced to 0°. These bombs will be called the "3.85-l. bomb" and "0.495-l. bomb," respectively.

Preparation of Catalysts.—Four catalysts well known for their use in hydrogenations in the moderate temperature range were prepared for comparison with cuprous oxide catalysts.

(1) **Cu-Ba-Cr Oxide.**[9]—A precipitate is formed by adding a solution of ammonium carbonate to a solution containing copper nitrate, barium nitrate and chromium-(III) nitrate. The precipitate is decomposed by heating to 230°. This catalyst is designated by "Cu-Ba-Cr-O-(C.F.A.) 230°."

(2) **Cu-Ba-Cr Oxide.**[10]—The Cu-Ba-Cr-O (C.F.A.) 230° catalyst is modified by suspension in a 10% solution of acetic acid, washing and drying at 110-120°. This catalyst is designated by "Cu-Ba-Cr-O (C.F.A.) washed."

(3) **The Cu-Ba-Cr-O** (C.F.A.) catalyst is decomposed at 160° instead of 230°. Its designation is "Cu-Ba-Cr-O (C.F.A.) 160°."

(4) **Cu-Cr Oxide.**[11]—Treatment of a solution containing copper sulfate and sodium dichromate with ammonium hydroxide produces a precipitate of $CuOHNH_4CrO_4$, which is decomposed at 200-400°. This catalyst is designated by "Cu-Cr-O (C.E.)."

The catalysts containing cuprous oxide were prepared in nearly all cases by grinding together, at room temperature, oxides of individual metals prepared separately. These oxides were prepared from chemicals of reagent grade or C. P. quality. The several ingredients were put into solution and the solutions were mixed slowly with constant stirring in the order indicated in the following directions, or treated as indicated.

(5) **Coprecipitated** Cu_2O **and** $Ca(OH)_3$.—One hundred fifty ml. of a 40% solution of sodium hydroxide is added to 43.8 g. of calcium nitrate, 100 g. of cupric nitrate trihydrate, and 100 g. of dextrose in 400 ml. of water. The mixture is heated to 85° for 30 min., filtered in a Büchner funnel, and washed until the wash water is clear. The precipitate is dried for 12 hr. in a vacuum desiccator, powdered and stored in a stoppered bottle.

(6) **Cu-Cr Oxide.**—A concentrated aqueous solution of CrO_3 is added to powdered $CuCO_3 \cdot Cu(OH)_2$ until effervescence ceases. To this solution, concentrated ammonium hydroxide is added until precipitation is complete. The precipitate is collected in a Büchner funnel, dried in air, pulverized, dried in a vacuum desiccator, heated to 160° and stored in a stoppered bottle.

(7) Cu_2O.—Two hundred fifty ml. of a 40% solution of sodium hydroxide is added to 1250 ml. of an aqueous solution of 250 g. of cupric nitrate trihydrate and 250 g. of dextrose. The mixture is digested for 30 min. at 85°, filtered in a Büchner funnel, and washed until the wash water is clear. The precipitate is dried *in vacuo* over anhydrone for 24-48 hr., powdered, dried for another 24 hr., and stored on a petri dish in a desiccator charged with phosphorus pentoxide. An analysis of the dark red product found 3.76% H_2O, 2.12% Cu and 94.12% Cu_2O.

(8) **CaO.**—Immediately before an experiment, a weighed sample of calcium hydroxide is ignited at 900-1000° until loss of weight indicates its conversion to calcium oxide (about 3 hr.), and cooled in a desiccator over phosphorus pentoxide.

(9) Cr_2O_3.—Three hundred ml. of concentrated ammonium hydroxide is added to 1 l. of an aqueous solution containing 250 g. of $Cr(NO_3)_3 \cdot 7.5H_2O$. The precipitate is collected in a Büchner funnel, dried 12 hr. at 110°, pul-

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[1] Abstracted in part from theses presented by Ralph E. Menzel, Meredith M. Stewart and Philip A. Lefrancois to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Adkins and Connor, This Journal, **53**, 1091 (1931).

[3] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

[4] Homer Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wis., 1937, p. 13.

[5] Adkins and Shriner, Catalytic Hydrogenation and Hydrogenolysis, Chap. 9 in "Organic Chemistry," Second Edition, Vol. I, Henry Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 788-789.

[6] Menzel, *Iowa State Coll. J. Sci.*, **12**, 142 (1937).

[7] Stewart, *ibid.*, **16**, 134 (1941), U. S. Patent 2,400,959 (1946).

[8] Lefrancois, *Iowa State Coll. J. Sci.*, **19**, 41 (1944).

[9] Connor, Folkers and Adkins, This Journal, **53**, 2012 (1931).

[10] Connor, Folkers and Adkins, *ibid.*, **54**, 1144 (1932).

[11] Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

verized, dried 4 hr. *in vacuo* at 450° and stored in a stoppered bottle.

(10) V_2O_4.—One hundred grams of V_2O_5 is added to 100 g. of glucose dissolved in 0.5 l. of water. The mixture is digested for 24 hr. on a steam plate. The precipitate is washed free from glucose, dried 12 hr. at 105°, powdered, dried *in vacuo* for 4 hr. and stored in a stoppered bottle. It is unlikely that the V_2O_5 is completely reduced to V_2O_4, or remains completely anhydrous.

Comparison of Catalysts and Promoters

The first set of experiments was carried out in the 3.85-l. bomb, using 8.6 g. of each of the four catalysts which were already recognized and four catalysts prepared by new methods. The bomb was charged with hydrogen at 500 p. s. i. and this was vented off to remove the greater part of the air before each experiment was started. In this series the bomb was charged with hydrogen at 1400 p. s. i., connected to the 220 volt circuit and heated to 237°. The current was then turned off. The pressure of the hydrogen was read at intervals of 5 min. and calculated to pressure at 0°. Figure 1 reports the data for this series of experiments.

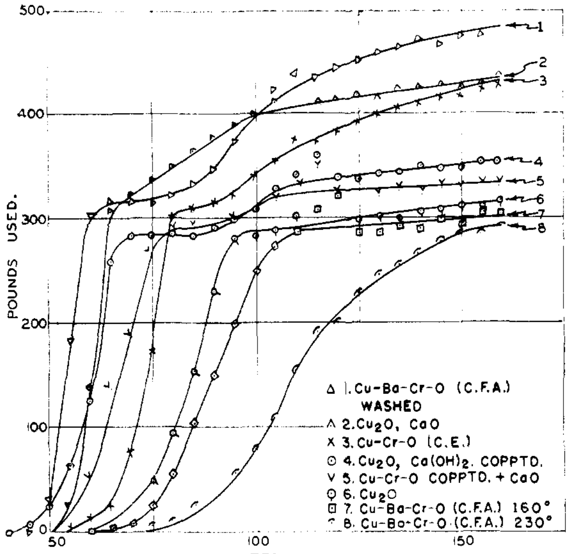

Fig. 1.—Decrease of pressure of H_2 in p.s.i. plotted against time in min. after heat was applied to the 3.85-l. bomb containing 3 moles of furfural, 8.6 g. of catalyst and H_2 at 1400 p.s.i.

A cuprous oxide catalyst promoted by calcium oxide was almost as active as Cu–Ba–Cr (C.F.A.) washed. This latter catalyst was so much better than the other established catalysts that it was used as a standard for comparison. This superiority was maintained whenever the others were used but no further report of their performances will be made.

Effects of Pressure of Hydrogen on Activity of Cuprous Oxide Catalysts.—The second series of experiments was designed to determine the effects produced by varying the pressure of the hydrogen in the presence of Cu_2O ground together with CaO. The curves in Fig. 2 show: (1) that the reaction starts at about the same interval of time after heating begins, for pressures from 600–1900 p. s. i.; (2) that for an initial pressure of 400 p. s. i. reaction occurs fairly rapidly down to about 170 p. s. i. and more slowly to 100 p. s. i.; (3) that pressures above 1000 p. s. i. add little to the rate of formation of furfuryl alcohol, but do increase the amount of hydrogen reacting after the three moles of furfural are converted to furfuryl alcohol.

Reproducibility of Data.—When the 0.495-l. bomb became available all factors which affect the rates of hydrogenation were studied and a series of four experiments were made in that bomb using an initial hydrogen pressure of 1000 p. s. i. and four independently prepared samples of a catalyst whose amount and composition were: 0.70 g. of Cu_2O, 0.70 g. of V_2O_4 and 0.525 g. of CaO.

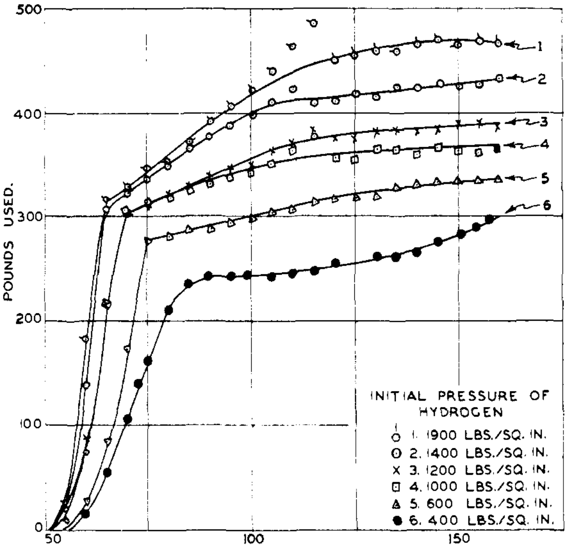

Fig. 2.—Each curve represents the cumulative decrease of the pressure of hydrogen in the 3.85-l. bomb, in p.s.i. plotted against time elapsed after heating started, with the initial pressure indicated, using 3 moles of furfural and 8.6 g. of the Cu_2O, CaO catalyst.

The procedure in the 0.495-l. bomb was changed to include (1) rocking the bomb at room temperature until the

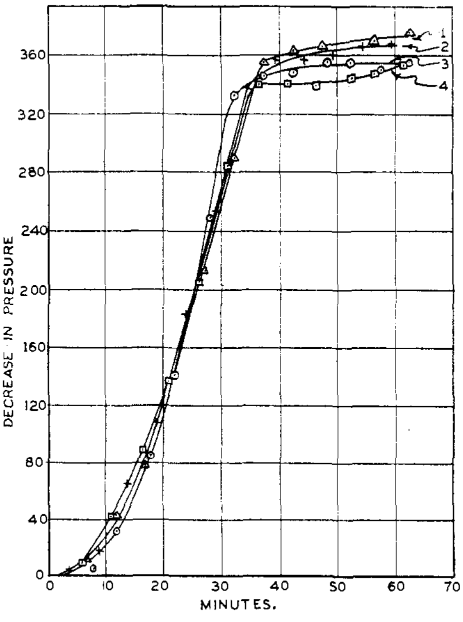

Fig. 3.—Reproducibility of results in 0.495-l. bomb. Graphs of decrease of pressure of hydrogen in p.s.i. against min. after decrease became measurable, for four independently prepared samples of the same catalyst (0.70 g. of Cu_2O + 0.70 g. of V_2O_5 + 0.525 g. of CaO) under a hydrogen pressure of 1000 p.s.i.

furfural was saturated and the pressure became constant (about 20 p. s. i. of hydrogen was absorbed), (2) while readings of pressure were made from the beginning of heating, the graphs report time in min. after decrease in pressure was detectable, (3) the heating was carried to only 200°, and (4) when cooling in air had caused a fall to 160°, the bomb was immersed in water to permit a second experiment to start with less delay. The reproducibility shown by Fig. 3 appeared satisfactory.

Optimum Proportions of Cu_2O, V_2O_4 and CaO.—It seemed unlikely that the first arbitrarily chosen composition of a three component catalyst would be the optimum composition. A mixture 0.7 g. of cuprous oxide and 0.575 g. of calcium oxide was arbitrarily chosen. Varying amounts of vanadium(IV) oxide were added in 7 steps from 0.00–1.00 g. These catalysts were tested in the 0.495-l. bomb under hydrogen at 1000 p.s.i. From the results reported in Fig. 4, the effects of the amounts of V_2O_4 between 0.30 g. and 0.70 g. were satisfactory.

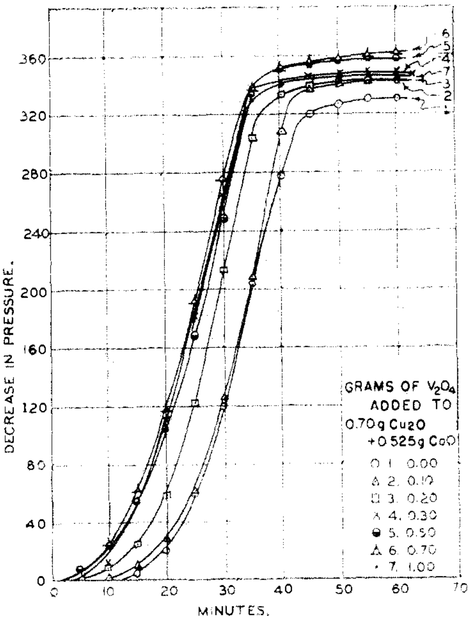

Fig. 4.—Effect of varying the weight of V_2O_4 in a Cu_2O, CaO catalyst. Decrease of pressure from 1000 p.s.i. plotted against time in min. after the decrease began, in the 0.495-l. bomb, for a catalyst containing 0.7 g. of Cu_2O, 0.525 g. of CaO and the weight of V_2O_4 indicated for each curve.

Choosing 0.70 g. of cuprous oxide and 0.5 g. of vanadium(IV) oxide the weights of calcium oxide were varied in 10 steps from 0.227 g. to 1.400 g. These 10 catalysts were tested under the same conditions as those described in the preceding paragraph, and the results are reported in Fig. 5. The curves show that 1.00–1.40 g. of CaO should be added to 0.70 g. of Cu_2O and 0.50 g. of V_2O_4 to produce the most effective catalyst.

Finally, 3 cuprous oxide catalysts of different compositions were compared to a sample of the Cu–Ba–Cr–O (C.F.A.) washed catalyst by subjecting 0.50 of a mole of furfural to hydrogen at a pressure of 1000 p. s. i. in the 0.495-l. bomb. The compositions and amounts of each catalyst, and the catalytic effect are reported by Fig. 6.

Each of the curves 2, 3 and 4 in Fig. 6 represents a rate of reaction produced by 1.75 g. of a catalyst under the same conditions. The catalyst formed by merely grinding together either cuprous oxide, chromium(III) oxide and calcium oxide, or cuprous oxide, vanadium(IV) oxide and calcium oxide produces a more rapid hydrogenation of furfural to furfuryl alcohol than an equal amount of the best of the copper chromium oxide catalysts. A comparison of curves 1 and 3 shows that the optimum proportions of vanadium(IV) oxide and calcium oxide added to 0.70 g. of cuprous oxide produce a still more rapid hydrogenation than the sample represented by curve 3.

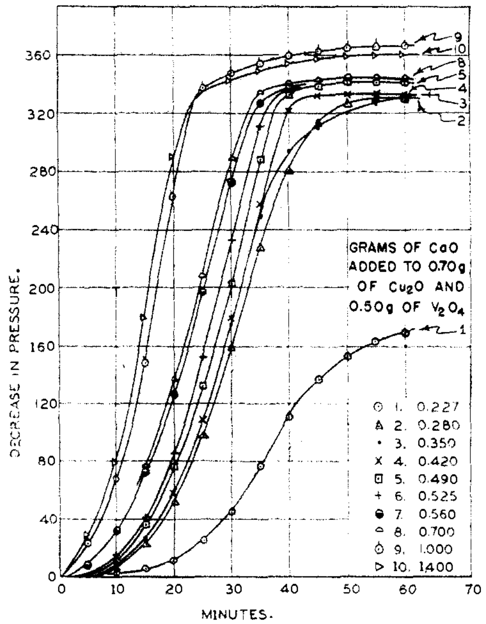

Fig. 5.—Effect of varying the weight of CaO in a catalyst containing 0.70 g. of Cu_2O and 0.50 g. of V_2O_4. Decrease of pressure from 1000 p.s.i. in p.s.i. is plotted against min. after decrease began in the 0.495-l. bomb for the weights of CaO indicated.

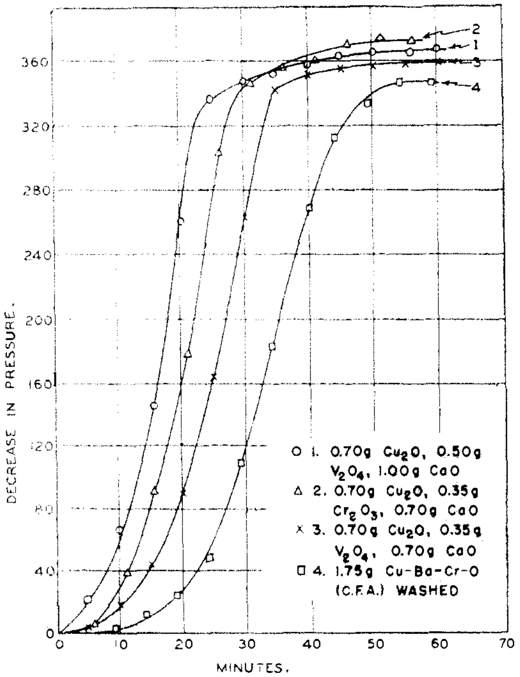

Fig. 6.—The rates of hydrogenation produced by three cuprous oxide catalysts compared to the rate produced by the best Cu–Cr–oxide catalyst.

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

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

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

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

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).