give for the heat of solution 7928 cal./mole with a probable error of ±15 (±0.19%) to give an average final concentration of 0.0495 *m*. Combining with the probable error of calibration we write

$$B_2O_3(\text{amorph.}) + \text{Aq.} = H_3BO_3(0.05\ m)$$
$$\Delta H = -7928 \pm 29 \text{ cal./mole}$$

The trend in heat of solution of B_2O_3 with changing final molality is smaller than with H_3BO_3. An extrapolation to infinite dilution gives for ΔH about −7960 cal./mole.

Two determinations were made of the heat of solution of glassy B_2O_3 prepared by fusion of H_3BO_3 in a platinum crucible. The average value of these was $\Delta H = -7963$ cal./mole at an average concentration of 0.0218 *m*.

The experimental results obtained for the molar heats of solution of B_2O_3 and H_3BO_3 may be combined to give the heat of conversion of B_2O_3 into H_3BO_3. We then obtain

$${}^1/_2B_2O_3(\text{amorph.}) + {}^3/_2H_2O = H_3BO_3(c)$$
$$\Delta H = -9130 \pm 39 \text{ cal./mole}$$

Summary

1. An isothermal calorimeter for measuring heats of solution and reaction in solution has been described. A unique feature is the use of a radar rectifying unit to supply the d.c. heating current for calibration.
2. Vacuum dehydration of crystalline H_3BO_3 to amorphous B_2O_3 has been described.
3. The molar heats of solution of H_3BO_3 and B_2O_3 to give 0.05 *m* solutions have been determined to be −5166 ± 36 and 7928 ± 29 cal./mole, respectively.
4. The heat of conversion of amorphous B_2O_3 to crystalline H_3BO_3 has been computed from these results to be 9130 ± 39 cal./mole of H_3BO_3.

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[CONTRIBUTION FROM THE MELLON INSTITUTE AND THE UNIVERSITY OF PITTSBURGH]

Equilibrium Measurements in the System C–CH_4–H_2[1]

BY L. C. BROWNING AND P. H. EMMETT

The carbon–hydrogen–methane equilibrium has been the subject of a number of investigations.[2,3,4,5,6] The experimental data are widely scattered, the disagreement being ascribed to such factors as temperature uncertainty, thermal diffusion and the use of different forms of carbon. Apparently the most reliable data are those[7] calculated from the thermodynamic properties of carbon (β-graphite), hydrogen and methane.

In the course of experiments relative to the iron–iron carbide–methane–hydrogen equilibria,[8] it was found that the carbon formed by the decomposition of iron carbide reacted readily with hydrogen at temperatures as low as 400°, the iron catalyzing the reaction. It therefore seemed worthwhile to study the carbon–hydrogen–methane equilibrium using carbon formed by this method, and to compare the results with those for the calculated equilibrium involving β-graphite. The present paper reports equilibrium constants for the reaction

$$CH_4 = C + 2H_2 \quad K_p = (H_2)^2/CH_4 \qquad (1)$$

in the range 380–838°.

Experimental

A synthetic ammonia iron catalyst was reduced at 500° in a stream of dry hydrogen. The iron was then carbided with normal butane at 275° to about 6% carbon and heated to 500° for 72 hours. Any Fe_3C remaining was removed by passing dry hydrogen over the sample at 275° at which temperature the Fe_3C is reduced rapidly while free carbon reacts relatively slowly. The 10-gram sample of iron catalyst after the above treatment contained about 0.57 g. of free carbon.

The apparatus and experimental procedure were essentially the same as those described in a previous paper.[7] At temperatures above 500° in the present case a clear quartz catalyst container was used instead of Pyrex glass, and a calibrated Pt-Pt, 10% Rh thermocouple was used for temperature measurement instead of a chromel–alumel couple. Also, provision was made for carbon dioxide analysis since it was found that at the higher temperatures the carbon reacted with a small amount of oxygen remaining on the iron to form CO and CO_2. The CO was converted to CO_2 by hot copper oxide during the hydrogen analysis, and the CO_2 determined by absorption on Ascarite. Correction was then made for the small amount of CO or CO_2 present in calculating the partial pressure of methane in the equilibrated gas sample.

Results and Discussion

The experimental values of log K_p are shown plotted against $10^3/T$ in Fig. 1. Some of the results obtained by other authors, and a curve representing the values as given by Rossini[7] are also included in Fig. 1.

If ΔC_p for reaction (1) is assumed to be the same as that for the reaction in which β-graphite is used as carbon, the variation of ΔC_p with temperature may be represented by the equation[9]

$$\Delta C_p = 9.18 - 5.96 \times 10^{-3}\,T - 0.051 \times 10^5\,T^{-2} \quad (2)$$

or, performing the proper integrations, the standard free energy for reaction (1) may be represented by the equation

$$\Delta F^\circ = \Delta H_0 - 21.14T \log T + 2.98 \times 10^{-3}T^2 + 0.026 \times 10^5 T^{-1} + IT \quad (3)$$

The integration constants ΔH_0 and I may be ob-

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[1] Joint contribution from the Gulf Research & Development Company's Multiple Fellowhsip, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Pa.

[2] (a) Bone and Jerden, *J. Chem. Soc.*, **71**, 41 (1897); (b) Pring and Hutton, *ibid.*, **89**, 1591 (1906).

[3] Coward and Wilson, *ibid.*, **115**, 1380 (1919).

[4] Pring, *ibid.*, **97**, 498 (1910).

[5] Schenck, *Z. anorg. allgem. Chemie*, **164**, 313 (1927).

[6] Randall and Mohammed, *Ind. Eng. Chem.*, **21**, 1048 (1929).

[7] Rossini, *et al.*, Circular of the National Bureau of Standards C 461 (1946).

[8] Browning, DeWitt and Emmett, THIS JOURNAL, **72**, 4211 (1950).

[9] Kelley, Bull. of Bur. of Mines No. 407 (1937).

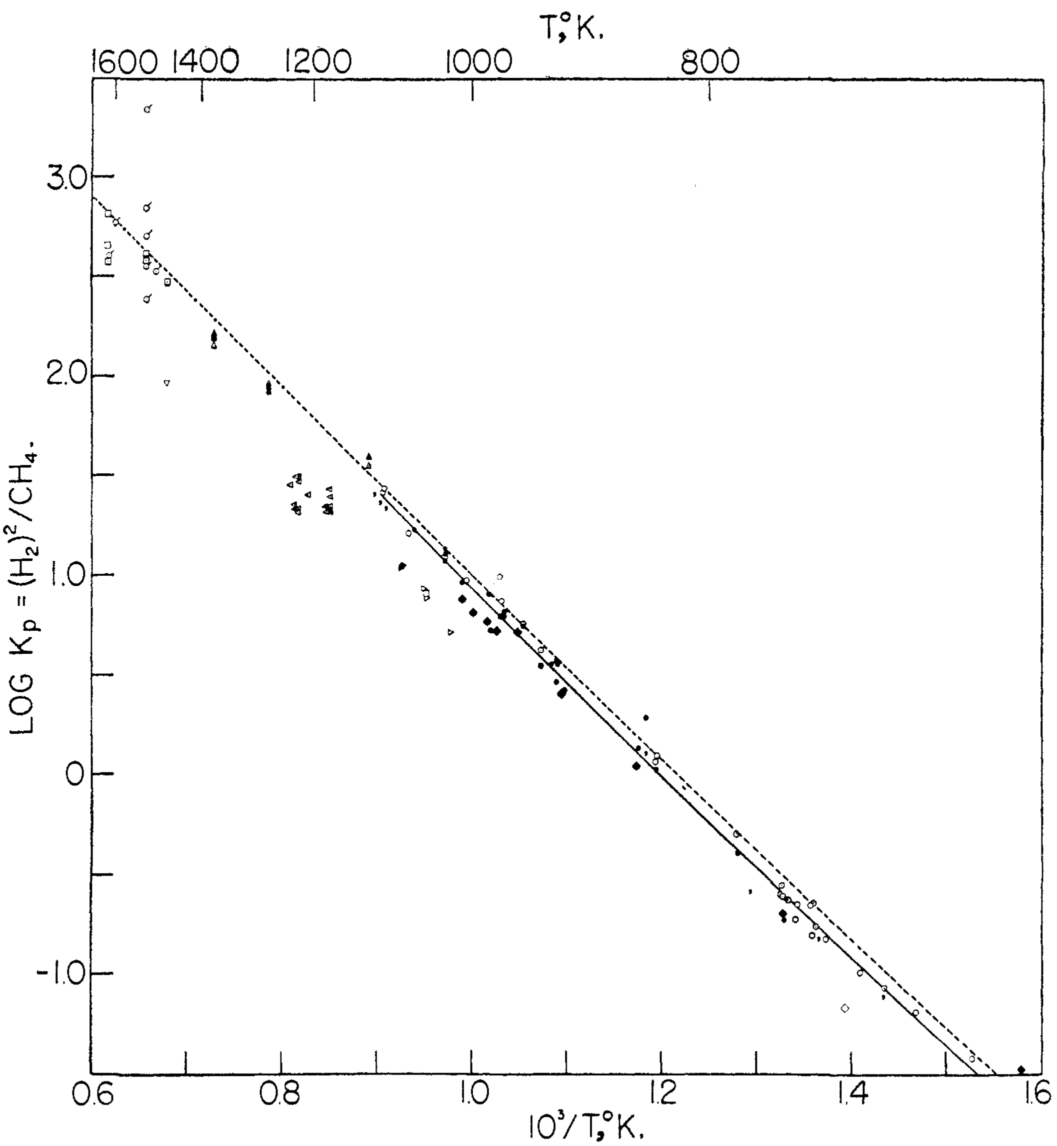

Fig. 1.—Log *Kp versus* $10^3/T$ for reaction (1): open symbols, equilibrium approached from excess hydrogen side; solid symbols, equilibrium approached from excess methane side: ▽, Bone and Jerden; ⊡, Pring and Hutton; ⊙, Pring; ◬, Coward and Wilson; ◇, Schenck; ⊲, Randall and Mohammed; O, authors' data; solid curve, authors' data; dotted line, calculated from Rossini.

tained from the experimental data by putting equation (3) in the form

$$\Sigma = -R \ln K_p + 21.14 \log T - 2.98 \times 10^{-3}T - 0.026 \times 10^5 T^{-2} = \Delta H_0/T + I \qquad (4)$$

The plot of Σ against $1/T$ yields a satisfactory straight line as determined by the method of least squares (shown in Fig. 2), the slope of which is ΔH_0 and the intercept of which is *I*. In the present case, these two values are 15,577 and 40.58, respectively. The standard free energy for reaction (1) may thus be represented by the equation

$$\Delta F^0 = 15{,}577 - 21.14T \log T + 2.98 \times 10^{-3}T^2 + 0.026 \times 10^5 T^{-1} + 40.58T \qquad (5)$$

In Table I are shown values of ΔF^0 calculated from equation (5) compared with values given by Rossini[7] for the standard free energy of decomposition of methane into hydrogen and carbon (β-graphite).

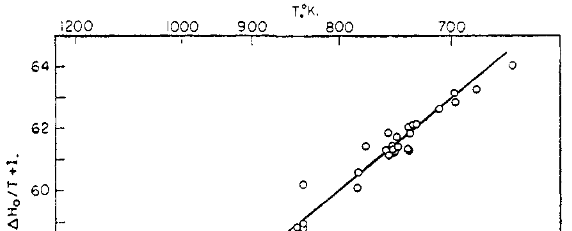

Fig. 2.—Σ *versus* $10^3/T$ for reaction (1).

The difference between the experimental and calculated values of the free energy listed in Table I

TABLE I

EXPERIMENTAL FREE ENERGY VALUES FOR REACTION (1) COMPARED WITH THOSE GIVEN BY ROSSINI FOR THE CORRESPONDING REACTION INVOLVING CARBON IN THE FORM OF β-GRAPHITE

	ΔF^0, kcal./mole	
T, °K.	Rossini	Authors' data
298.16	12.140	12.353
300	12.105	12.318
400	10.048	10.284
500	7.841	8.092
600	5.490	5.764
700	3.050	3.345
800	0.550	0.854
900	−2.010	−1.691
1000	−4.610	−4.280
1100	−7.220	−6.901

is such as to indicate that the carbon used in the present work is thermodynamically unstable with respect to β-graphite, and that the free energy change per mole for the conversion of the carbon here used to β-graphite is about 300 calories. This seems reasonable since one would not have expected the carbon used in the present work to have graphitized at even the highest experimental temperature employed. The numerical value for the free energy change for the conversion of the carbon used in the present work to graphite must, however, be considered as only approximate since it is the difference between two large values for free energy.

Since the completion of this work it has been noted that Troesch[10] has obtained equilibrium values for reaction (1) for carbon supported on a nickel catalyst at temperatures as low as 143°. The equilibrium constants obtained by Troesch in the range 143–252° are low compared to Rossini's values by a factor of about 2. The present data extrapolated to these low temperatures give values of the equilibrium constant which are low compared to Rossini's values by a factor of about 1.5.

Summary

Equilibrium constants for the reaction $CH_4 = C + 2H_2$ have been measured in the temperature range 380–838°, the carbon present being formed from the decomposition of Fe_3C. The values obtained are close to those for the reaction in which the carbon form is β-graphite.

[10] Troesch, International Conference on Heterogeneous Kinetics at Lyon, France, September, 1949.

PITTSBURGH 13, PENNSYLVANIA RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LOUISVILLE]

Chelate Formation between Copper and 8-Quinolinols

BY J. P. PHILLIPS AND F. J. O'HARA

As part of a study of practical applications of chelate stability principles the lines of investigation described here were tried, using various substituted 8-quinolinols as the chelating agents. Cupric ion was selected as the chelating metal because it apparently forms more stable chelates than other common metals.

Experimental

Reagents.—The preparation and purification of the 8-quinolinols have been previously described.[1,2] Standard solutions of cupric ion were made from weighed amounts of copper foil dissolved in nitric acid; for the conductometric titrations solutions of copper sulfate were used after standardization by electrodeposition.

Complex Formula Determination.—The formula of the soluble complex between copper and 8-quinolinol-5-sulfonic acid was determined spectrophotometrically by the method of continuous variations.[3] All measurements were taken with a Beckman model DU spectrophotometer, using 1.00 cm. cells. The experiment was made with 0.0158 M solutions in 2 M ammonium hydroxide at 460 mμ, and again with 0.0119 M solutions in a potassium acid phthalate buffer of pH 4.0 at 560 mμ. After the formula was determined, the extinctions of 0.0053 M solutions of the complex at various pH values were measured at 620 mμ, where the components of the complex had a negligible absorption, in order to obtain an estimate of the range of pH over which the complex formed.

Conductometric Titrations.—A standard solution of 8-quinolinol in isopropyl alcohol was added from a microburet to known volumes of 0.0166 M copper sulfate diluted to a total volume of 200 ml. The conductivities were measured after each addition of the standard solution using a dip type cell (having a cell constant of about 0.44) with an Industrial Instruments Conductivity Bridge, Model RC-1B. Since the amount of standard solution added was less than 2% of the total volume, no dilution corrections were made.

Mohr-type Titrations.—Fifty ml. of a solution containing 0.00658 g. of cupric ion in an acetate buffer of pH 4.4 and 0.1 ml. of 1% ferric iron as indicator was titrated with a 0.0201 M solution of 8-quinolinol in 50% alcohol until a black coloration persisted in the solution. A blank correction amounted to less than 0.1 ml.

A similar titration was carried out using 0.5 ml. of a 1% aluminum solution as indicator, the end-point being detected by the appearance of a fluorescence under ultraviolet light. The blank correction amounted to 0.25 ml. for a total solution volume of about 50 ml.

Results and Discussion

Relative Stabilities.—The relative stabilities of the copper chelates formed by 8-quinolinol, 2-methyl-8-quinolinol, 4-methyl-8-quinolinol and 8-quinolinol-5-sulfonic acid were established by means of a series of competitive reactions. Equivalent amounts of 8-quinolinol and the 2-methyl derivative were added simultaneously to an ammoniacal solution containing insufficient cupric ion to react with both; the resulting precipitate was filtered off, dissolved in chloroform and the ultraviolet absorption spectrum determined. Since the spectrum was that of the 8-quinolinol copper salt rather than that of the 2-methyl-8-quinolinol salt,[4] it appeared that 8-quinolinol formed the more stable chelate. A similar competition between 8-quinolinol and the 4-methyl derivative was won by the 4-methyl compound. The determination of the

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[1] Phillips, Elbinger and Merritt, THIS JOURNAL, **71**, 3986 (1949).

[2] Matsumura, *ibid.*, **49**, 810 (1927).

[3] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

[4] Phillips and Merritt, *ibid.*, **71**, 3984 (1949).