

and Voge^{1b} state that they have obtained samples with a specific conductivity of 1.05×10^{-8} mhos. We have found that acid of specific conductivity of about 0.60×10^{-8} mhos may be prepared in quantity without undue difficulty. Recently acid with a specific conductivity as low as 0.40×10^{-8} mhos has been prepared in this Laboratory. Our work would indicate that the influence of small amounts of moisture, responsible for the slight variations in the specific conductivity of the solvent, is without appreciable effect on the

conductivities of solutions except possibly in the very dilute range.

Summary

1. Anhydrous acetic acid has been prepared in quantity with a specific conductivity at 25° of 0.60×10^{-8} mhos.

2. The specific conductances of dilute sulfuric acid solutions in this acid as well as in acid of somewhat higher specific conductivity have been determined.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, YALE UNIVERSITY]

The Equilibrium between Carbon Monoxide, Hydrogen, Formaldehyde and Methanol.¹ II. The Reaction $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

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Introduction

In the course of some experiments undertaken primarily to determine the conditions of equilibrium in the synthesis of formaldehyde from carbon monoxide and hydrogen, it was possible at the same time and by some additional experiments in the same apparatus to secure further data on the equilibrium conditions in the methanol synthesis reaction. Although the equilibrium constants for this reaction have been measured by a number of investigators, the results are not very concordant and further work was desirable. Part of the lack of agreement may be attributed to (1) the use of different thermal data for the interpolation and extrapolation of the equilibrium constant with respect to temperature and (2) the difficulties involved in reducing the measurements to a common pressure. The publication of some new thermal data and an increase in our knowledge of the effect of pressure on the equilibrium constant was a further justification for a paper on this subject.

This equilibrium constant may be calculated from those obtained for two other reactions, namely, $\text{CO} + \text{H}_2 \rightleftharpoons \text{HCHO}$, and $\text{HCHO} + \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$, which have been measured by the authors.² However, the measurements for these two reactions were not made at the same temperature, and the thermal data for formalde-

hyde are so doubtful that the equations given in the earlier paper can only be considered as order of magnitude results and the values of the Kp for this reaction derived from them would be far less accurate than actually measured data for the reaction in question. It seemed therefore desirable to continue the earlier work at 3 atmospheres total pressure and over a temperature range of 225 to 275° to measure directly the equilibrium constant in the methanol equilibrium.

Review of Previous Work

The previous work on the methanol equilibrium has been very well summarized by Parks and Huffman³ and a table of the values observed at the various temperatures and pressures and the calculated values of Kp_0 (equilibrium constant at low pressure) is all that will be given here. In Table I, the factor given for the conversion of Kp at the measured temperature and pressure, to Kp_0 , at the same temperature, is derived by a method (to be published shortly) based on the assumptions that the partial fugacity rule of Lewis and Randall⁴ holds for this case, and that the activity coefficient (ratio of fugacity to pressure) for any gas is a function of the reduced pressure and reduced temperature only. These assumptions appear to be justified for the ammonia equilibrium, for which accurate data are available.

(3) "Free Energies of Some Organic Compounds," A. C. S. Monograph No. 60.

(4) Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923.

(1) This paper is based on a Dissertation presented by R. H. Newton in June, 1933, to the Faculty of the Graduate School of Yale University, in candidacy for the degree of Doctor of Philosophy.

(2) Newton and Dodge, *THIS JOURNAL*, **55**, 4747 (1933).

TABLE I
RESULTS OF PREVIOUS INVESTIGATORS ON THE METHANOL
EQUILIBRIUM

Investigator ^a	Temp., °C.	Pres- sure, atm.	K_p $\times 10^4$ observed	Factor	K_p $\times 10^4$
Von Wettberg and Dodge	329	170	1.4	0.52	0.73
	300	170	1.8	.46	0.83
	302	170	3.2	.47	1.5
	301.5	170	3.0	.47	1.41
	309	170	1.5	.48	0.72
	302	170	4.3	.47	1.82
	258.5	170	129	.33	43.0
	259	170	84	.33	28.0
	274	170	37	.38	14.1
	273	170	29	.38	11.0
	307	170	4.3	.48	2.1
	258	170	48	.33	28.0
298	170	11	.45	5.0	
Audibert and Raineau	400	50	0.192	.67	0.13
Lewis and Frolich	400	204	.180	.58	.11
Brown and Gallo- way	400	180	.162	.62	.10
	400	180	.198	.62	.12
Smith and Hirst	304	1	3.8	1.00	3.8
	304	1	6.7	1.00	6.7
	304	1	2.4	1.00	2.4
	304	1	3.67	1.00	3.67
Smith and Bran- ting	303.8	1	5.57	1.00	5.57
Lacy, Dunning and Storch	250	50	11.7	0.72	8.4
	300	50	1.80	.81	1.5
	250	20	18.0	.88	15.8
	200	50	296	^a	
	295	64.5	2.2	0.74	1.6
Newitt, Byrne and Strong	310	69.3	1.6	.76	1.2
	330	76.5	0.52	.74	0.39
	280	88.1	4.5	.60	2.7
	289	100.1	3.0	.58	1.7
	306	97.1	1.3	.65	0.85
	320	96.1	0.66	.78	.44
	338	93.8	.45	.71	.31

^a The method used does not permit the calculation of this factor for temperatures below the critical temperature for any component.

Experimental Part

The apparatus, procedure and methods of analysis for the equilibrium measurements have been described elsewhere.² In general, the runs were not as long as those used in the determination of the formaldehyde equilibrium since no great amount of condensate was necessary to obtain an accurate analysis for methanol.

The catalysts used in this study were numbers

(5) Von Wettberg and Dodge, *Ind. Eng. Chem.*, **22**, 1040 (1930); Audibert and Raineau, *ibid.*, **20**, 1105 (1928); Lewis and Frolich, *ibid.*, **20**, 285 (1928); Brown and Galloway, *ibid.*, **20**, 960 (1928); Smith and Hirst, *ibid.*, **22**, 1037 (1930); Smith and Branting, *This Journal*, **51**, 129 (1929); Lacy, Dunning and Storch, *ibid.*, **52**, 926 (1930); Newitt, Byrne and Strong, *Proc. Roy. Soc., (London)*, **A123**, 236 (1928).

1, 11 and 12 (molal compositions CuZn_3 , CuZn_2 , and CuZn , respectively) and the details of their preparations have been given in the paper referred to.

Liquid air was used as the cooling medium for all runs, to ensure complete condensation of the methanol product.

Twenty-seven runs (about one-half of which were in the decomposition direction) were made at approximately 3 atmospheres total pressure and at temperatures of 225, 250 and 275°. The results are summarized in Table II.

TABLE II
EXPERIMENTAL RESULTS FOR THE METHANOL
EQUILIBRIUM

Run ^a	Temp., °C.	Space ve- locity ^b	Press., atm.	Dura- tion of run, hrs.	Grams of methanol		$K_p \times 10^4$
					Titration	Colori- metric	
82	225	9.2	3.01	7.0	0.1552	0.1547	5.13
83 ^D	225	13.2	3.00	13.1	0.3860	0.3880	7.08
84	225	18.8	3.01	55.0	2.915	2.910	6.05
85 ^D	250	25.0	2.98	5.2	0.0823	0.0820	1.59
81 ^D	250	12.3	3.00	17.7	.2279	.2271	2.03
80 ^D	250	22.2	3.00	7.5	.1512	.1658	1.16
79	250	10.4	3.01	17.5	.2210	.2220	2.34
78	250	8.1	3.01	21.7	.1353	...	1.45
77	250	7.4	3.01	45.8	.2860	...	1.64
76	250	4.5	2.99	19.5	.0891	...	2.03
75 ^D	250	3.2	3.02	22.0	.0705	...	1.97
74 ^D	250	10.5	3.01	4.0	.1120	...	2.40
73 ^D	250	2.5	3.01	16.7	.0459	...	2.20
72 ^D	250	14.0	3.02	6.0	.0424	...	0.98
71 ^D	250	7.4	3.00	17.8	.1398	...	2.09
70 ^D	250	13.2	2.98	12.0	.1438	...	1.90
69 ^D	250	18.1	3.03	5.3	.0579	...	1.28
66 ^D	250	16.5	3.01	6.0	.0744	...	1.62
64	250	8.9	3.00	31.3	.5780	...	4.92
63	250	14.8	3.02	14.4	.4240	...	5.20
58	250	6.4	3.05	27.5	.2175	.2070	2.64
57	250	14.0	3.03	9.6	.0996	.0949	1.73
65	251	6.3	3.02	34.0	.4381	...	4.73
59	275	13.6	3.05	20.0	.1161	.1000	1.00
60	276	11.9	3.04	20.0	.0941	.0800	0.88
61	276	7.1	3.02	37.3	.1115	.0980	1.00
62	277	15.4	3.02	17.0	.0800	.0730	0.66

^a D indicates methanol decomposition run. ^b Liters of exit gas (at standard conditions) per liter of catalyst volume per hour.

Discussion and Correlation of Results

A blank run was made using the same inlet gas as was used in the other runs, but with no catalyst in the reactor. No condensate was obtained in this case, showing that the relatively small amounts of methanol formed in the reaction were due to actual synthesis. The methanol saturator was calibrated by passing gas through it at the

rate used in the equilibrium runs and with no catalyst in the reactor. This test showed that there was approximately ten times the equilibrium concentration of methanol in the gas entering the reactor for the decomposition runs.

It was noticed that the total weight of condensate was greater than the weight of methanol in nearly all cases. Since methyl formate was shown to be absent, it was thought that this might be due to the formation of higher alcohols, which floated as an oil on the surface of the water layer when the condensate was diluted for analysis. Hence, the combined water layers of the condensates for all runs were fractionated in a vacuum jacketed micro-distillation column, and 1.6 cc. of methanol (boiling point 64°) was obtained. The boiling point curve was nearly identical with that obtained in fractionating a mixture of the same volume containing 1.6 cc. of absolute methanol in distilled water, and the "break" in these two curves was much sharper than in that obtained by fractionating a similar mixture containing 0.1 cc. of normal propanol, indicating that no appreciable quantity of this higher alcohol was present, and that the condensates were essentially methanol and water. The oil layers were similarly united and fractionated and, in this case, the initial boiling point was 102°, indicating that methanol was absent in this layer. A further indication of the absence of compounds other than methanol and water is the excellent checks obtained between the colorimetric and titration methods for determining methanol.

The temperature throughout the catalyst did not vary more than 0.1° from the figure given in Table II as shown by calibrated thermocouples placed at different locations in the catalyst bed. The temperature did not vary with time more than 0.1°, as shown by accurate temperature records taken with a recording potentiometer.

To correlate the values obtained at different temperatures the following data were chosen: for methanol^{3,6}

$$C_p = 2.0 + 0.03 T$$

$$\text{Heat of combustion}^7 \Delta H = -173,610$$

$$\text{Entropy of liquid at } 25^\circ = 30.3 \text{ E. U.}^8$$

(6) The nomenclature of Lewis and Randall is used throughout.

(7) Rossini, *Proc. Nat. Acad. Sci.*, **17**, 343 (1931).

(8) Kelley, *THIS JOURNAL*, **51**, 181 (1929).

for hydrogen^{9,10}

$$C_p = 6.65 + 0.00070 T$$

$$\text{Heat of combustion}^{11} \Delta H = -68,313$$

$$\text{Entropy at } 25^\circ \text{ and } 1 \text{ atm.} = 31.25 \text{ E. U.}^{12}$$

for carbon monoxide

$$C_p^9 = 6.89 + 0.00038 T$$

$$\text{Heat of combustion}^{13} \Delta H = -67,623 \text{ (at } 25^\circ)$$

$$\text{Heat of combustion}^{14} \Delta H = -68,100 \text{ (at } 18^\circ)$$

$$\text{Entropy at } 25^\circ \text{ and } 1 \text{ atm.} = 47.3 \text{ E. U.}^{15}$$

$$\text{Entropy at } 25^\circ \text{ and } 1 \text{ atm.} = 45.9 \text{ E. U.}^{12}$$

Using these values, four equations result, depending on which entropy and which heat of combustion of carbon monoxide are chosen. These are

$$\log_{10} Kp_0 = 3838/T - 9.1293 \log_{10} T + 0.00308 T + 13.112 \quad (\text{A})^{16}$$

$$\log_{10} Kp_0 = 3828/T - 9.1293 \log_{10} T + 0.00308 T + 13.412 \quad (\text{B})^{17}$$

$$\log_{10} Kp_0 = 3724/T - 9.1293 \log_{10} T + 0.00308 T + 13.112 \quad (\text{C})^{18}$$

$$\log_{10} Kp_0 = 3724/T - 9.1293 \log_{10} T + 0.00308 T + 13.412 \quad (\text{D})^{19}$$

The deviation of the equilibrium constant at three atmospheres from Kp_0 is calculated to be 1.5% at 250°, which is negligible compared to experimental errors, so no correction has been applied for the effect of pressure.

The correlation of results is shown in Fig. 1, where the experimental points of all investigators are shown together with the values given by the four equations. The agreement between the averages for a given temperature of the values measured in this work and equation D seems excellent, as shown in Table III, and inasmuch as this equation fits the values obtained by all other investigators as well as any of the equations, it appears to be the best representation of the points.

(9) Partington, "Specific Heat of Gases," Ernest Benn, London, 1924.

(10) The equations of Partington were chosen because they were simpler than the more accurate equations of Eastman [Bureau of Mines, Information Circular No. 445 (1924)], although the deviation between the two sets is less than 2% in the temperature range of 25 to 525°.

(11) Rossini, *Proc. Nat. Acad. Sci.*, **16**, 694 (1930).

(12) Kelley, *Ind. Eng. Chem.*, **21**, 353 (1929).

(13) Rossini, *Bur. Standards J. Research*, **6**, 37 (1931).

(14) Thomsen, "Thermochemische Untersuchungen," 1886, Vol. II, p. 2881.

(15) Clayton and Giaque, *THIS JOURNAL*, **54**, 2610 (1932).

(16) Entropy of carbon monoxide from Giaque and heat of combustion from Rossini.

(17) Entropy of carbon monoxide from Kelley, heat of combustion from Rossini.

(18) Entropy of carbon monoxide from Giaque, heat of combustion from Thomsen.

(19) Entropy of carbon monoxide from Kelley, heat of combustion from Thomsen.

TABLE III
COMPARISON OF OBSERVED VALUES OF EQUILIBRIUM
CONSTANTS WITH EQUATION (D)

Temp., °C.	$Kp \times 10^3$ obs.	$Kp \times 10^3$ calcd. by Equation (D)
225	6.08	6.3
250	2.32	2.2
276	0.88	0.80

It should be pointed out that the molal heat capacity of methanol vapor is somewhat in doubt

The fact that equation D fits our experimental points better than any of the other equations must not be construed as offering any proof of the greater accuracy of the particular thermal data involved. For example, equation D involves Thomsen's heat of combustion of carbon monoxide, whereas there is every reason to believe that the value of Rossini is more accurate. Another equation could readily be obtained which

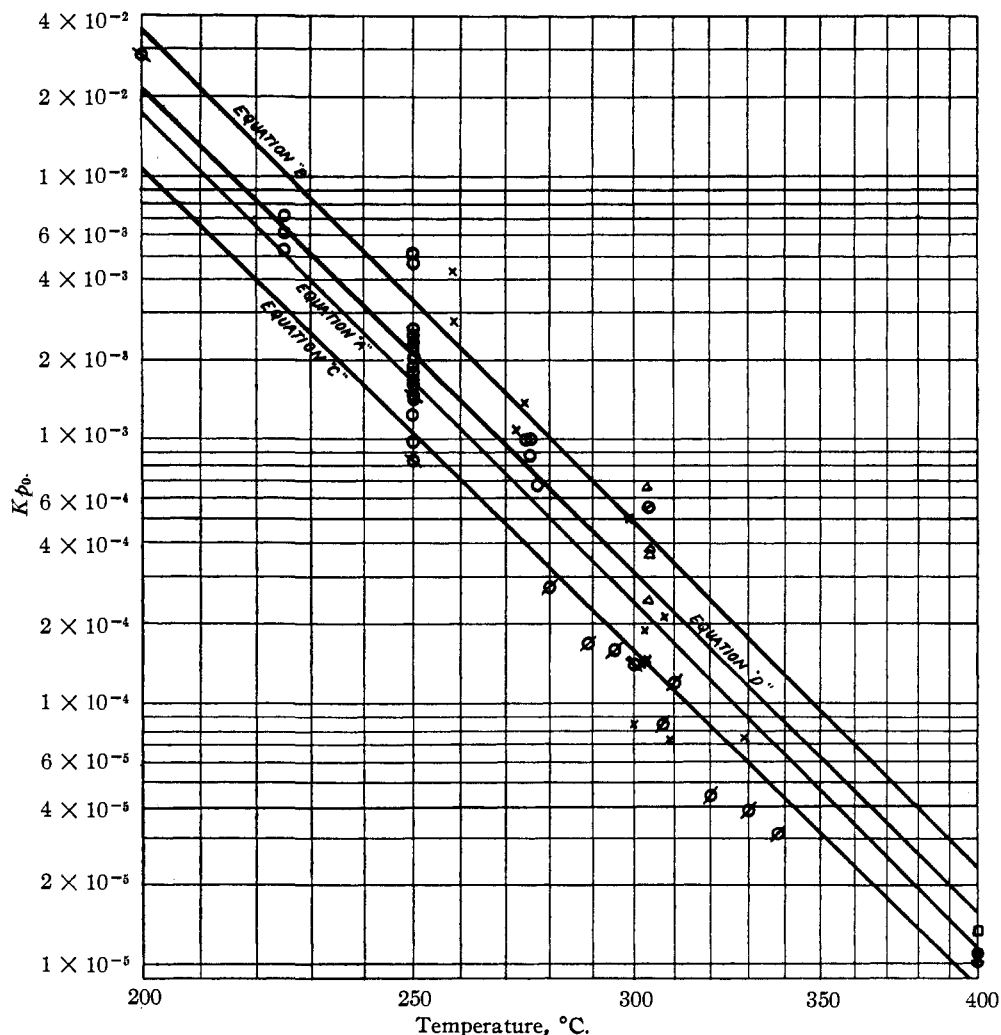


Fig. 1.—Plot of Kp_0 vs. temperature: X, von Wettberg and Dodge; □, Audibert and Raineau; ●, Lewis and Frolich; ▽, Brown and Galloway; △, Smith and Hirst; ⊙, Smith and Branting; ⊘, Lacy, Dunning and Storch; ⊚, Newitt, Byrne and Strong; ○, Authors.

and this may affect the choice of the other thermal data to get the best fit with the experimental points. However, the use of the equation for the molal heat capacity of methanol proposed by Francis²⁰ leads to only a very slight change in the location and slope of the curves.

(20) Francis, *Ind. Eng. Chem.*, **20**, 283 (1928).

used Rossini's value and also fitted the experimental points just as well as equation D, merely by using a different value for the entropy of carbon monoxide, or of methanol or of the heat of combustion of methanol. The object in giving those four equations is to show how much of a spread can be produced merely by different choices of

thermal data. Even if the equilibrium data were extremely accurate they would not permit one to predict greater reliability for any particular datum because each equation involves a combination of several data. Equation D must, therefore, be regarded largely as an empirical equation which best represents the experimental points.

It should also be noted that none of the catalysts used was specific for the reaction in question, and hence side reactions such as the formation of methane or higher alcohols may have affected the values obtained. It would appear impossible to

obtain closer agreement among the measured values of the equilibrium constant until a much more specific catalyst is found.

Summary

The equilibrium $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ has been investigated at temperatures of 225, 250 and 275° at a pressure of three atmospheres. The values obtained agree with the following theoretical equation, which is based on some of the most reliable thermal data available

$$\log_{10} Kp_0 = 3724/T - 9.1293 \log_{10} T + 0.00308 T + 13.412$$

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Dipole Moments of Some Mono Substitution Products of Mesitylene

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Mesitylene compounds with substituents in the ring afford an unusual opportunity for studying the effects of the interaction of methyl groups with other substituents as reflected in the dipole moment values. The inherent moments due to the three methyl groups because of their symmetrical location in the ring cancel each other and allow of a study of the interactions between the methyl groups and the other substituent which is fairly free of the complicating factors usually present in molecules of this complexity. This paper gives the results of the measurements of the dipole moments of fluoro-, chloro-, bromo- and iodomesitylene and of nitromesitylene and mesitol.

Method and Apparatus.—Details of the experimental procedure and apparatus used will be found in previous papers.^{1,2}

Materials.—The benzene and carbon tetrachloride used as solvents were purified as previously described.^{1a}

Fluoromesitylene.—Mesityldiazonium borofluoride was prepared from mesidine hydrochloride by the method of Wilke-Dörfurt and Balz³ and then decomposed by heating according to the procedure of Balz and Schiemann⁴ to give fluoromesitylene which was purified by distillation, washing with sodium hydroxide, drying and refractionating four times. A sample with b. p. 168.5–168.7° was used.

Chloromesitylene was made by direct chlorination using a modification of the method of Fittig and Hoogewerff.⁵

Chlorine and mesitylene were brought together at the lower end of a narrow inclined glass tube surrounded with cold brine, the gas bubbles carrying the mixture of chloromesitylene and mesitylene over into a trap filled with 5% sodium thiosulfate solution to prevent further reaction. The mixture separated from this was washed with 15% sodium hydroxide solution to remove residual acid and hydrolyze any side chain derivatives and then was washed with water, dried and distilled. The purified fraction used boiled from 103.6 to 103.7° at 25 mm.

Bromomesitylene was prepared by the method of Smith.⁶ A sample with b. p. 119.2–119.3° at 25 mm. was used for the measurements.

Iodomesitylene.—This was prepared by the method of Datta and Chatterjee,⁷ washed with 15% sodium hydroxide, with water, with sodium thiosulfate, followed by repeated recrystallization from alcohol giving a product which froze at 30.0°.

Nitromesitylene.—This was prepared by the method of Bamberger and Rising⁸ with slight modifications and was purified by recrystallization from alcohol and by fractional crystallization; f. p. 43.0–43.2°.

Mesitol.—Mesidine hydrochloride was diazotized and the diazonium compound hydrolyzed in the usual manner to mesitol. The sample was recrystallized twice from petroleum ether; f. p. 71.5–71.8°.

Results.—In Table I are given the results of the density and refractive index measurements on the halogen substituted mesitylenes all of which could be measured as liquids at 30°. The last column gives the calculated molecular refractivity for the sodium D line. This information is not in the literature and so is included here.

(6) Smith, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 24.

(7) Datta and Chatterjee, *THIS JOURNAL*, **39**, 438 (1917).

(8) Bamberger and Rising, *Ber.*, **33**, 3625 (1901).

(1) (a) de Bruyne, Davis and Gross, *THIS JOURNAL*, **55**, 3936 (1933); (b) *Physik. Z.*, **33**, 719 (1932).

(2) Gross, *ibid.*, **32**, 587 (1931).

(3) Wilke-Dörfurt and Balz, *Ber.*, **60**, 115 (1927).

(4) Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

(5) Fittig and Hoogewerff, *Ann.*, **150**, 323 (1869).