[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROESSLER AND HASSLACHER CHEMICAL COMPANY]

EQUILIBRIUM IN THE SYNTHESIS AND DECOMPOSITION OF METHANOL

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RECEIVED SEPTEMBER 23, 1929 PUBLISHED MARCH 6, 1930

Introduction

Attempts to obtain values of equilibrium constants for the reaction

$$2H_2 + CO = CH_3OH \qquad (I)$$

have been made in three ways, *viz.:* calculations based on measurements of equilibria in the two reactions

$$2H_2 + HCOOCH_3 = 2CH_3OH \qquad (II)$$
$$CH_3OH + CO = HCOOCH_3 \qquad (III)$$

calculations based on measurements of the specific heat of methanol down to liquid hydrogen temperatures and the third law of thermodynamics and, finally, direct experimental measurement of the equilibrium concentrations of the three gases. The first method was employed by Christiansen.[1] His measurements were admittedly of a preliminary character. Additional measurements of equilibria in Reactions II and III have been made by one of the authors and will be presented in this paper. The second method has been employed by Kelley[2,3] and by Smith,[4] their calculations being based on the specific heat data of Parks[5] and Kelley.[6] The third method may be subdivided into two types of experiments, *viz.:* those in which the measurement of equilibrium is made from the synthesis side only, the primary object being to test catalysts for their activity, and those in which measurements from both the synthesis and decomposition sides are made, the primary object being to obtain reliable equilibrium data.

In the first subdivision of the third method may be grouped experiments and calculations of Audibert and Raineau,[7] Lewis and Frolich,[8] Brown and Galloway[9] and Fieldner and Brown.[10] In the second subdivision should be placed the experimental work of Smith and Branting,[11]

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[1] Christiansen, *J. Chem. Soc.*, 413 (1926).

[2] Kelley, *Ind. Eng. Chem.*, **18**, 78 (1926).

[3] Kelley, *ibid.*, **21**, 353 (1929).

[4] Smith, *ibid.*, **19**, 801 (1927).

[5] Parks, THIS JOURNAL, **47**, 338 (1925).

[6] Kelley, *ibid.*, **51**, 180 (1929).

[7] Audibert and Raineau, *Ind. Eng. Chem.*, **20**, 1105 (1928).

[8] Lewis and Frolich, *ibid.*, **20**, 285 (1928).

[9] Brown and Galloway, *ibid.*, **20**, 960 (1928).

[10] Fieldner and Brown, *ibid.*, **20**, 1110 (1928).

[11] Smith and Branting, THIS JOURNAL, **51**, 129 (1929).

Newitt, Byrne and Strong[12] and the data to be presented below on the direct measurement of equilibrium in Reaction I.

The results obtained by the first and third methods of estimating the equilibrium constants of Reaction I are of the same order of magnitude (they agree within a factor of about 3). These results are, however, 10 to 50 times smaller than the lowest values obtained by the second method, *i. e.*, by way of the specific heat data on methanol and the third law of thermodynamics. This discrepancy has thus far not been explained.[12a] In view of the recent determination of the entropy of methanol by Kelley,[6] whose value checks the earlier determination by Parks,[5] attention should be focused on other possible sources of error, such as a constant error in determining the entropy of methanol, or errors in the estimation of the entropies of hydrogen and oxygen.

The results presented in this paper were completed about eighteen months before the appearance of Smith and Branting's[11] paper. Although the authors' work does not furnish any clue to the source of the discrepancy mentioned above, the data furnish more reliable figures on equilibrium Reactions II and III, as well as additional confirmatory data on Reaction I. The experiments of Smith and Branting[11] were made at atmospheric pressure and at about 300°. The quantities of methanol in the equilibrium mixture at atmospheric pressure were very minute, necessitating sensitive colorimetric tests. The data of Newitt, Byrne and Strong[12] were obtained at 100 and at 70 atmospheres' pressure, the temperatures ranging from 280 to 338°. The quantities of methanol under these conditions were sufficient to permit the preparation of an easily identified derivative of methanol. The authors' measurements were made at 50 and at 20 atmospheres' pressure and at temperatures of 200, 250 and 300°. The amounts of methanol obtained from the equilibrium mixtures under these conditions were considerably larger than those of Newitt, Byrne and Strong, and were sufficient to permit qualitative and quantitative analysis (the latter involving fractional distillations). Due to the pressure of other work, it was not possible to make the measurements as complete or over as extended a range as could have been desired.

Calculations Via the Methyl Formate Reactions.—In some unpublished work done in 1922 by one of us, the equilibria of Reactions II and III were measured. Christiansen[1] also measured these at a later date. The experimentally determined constants of both observers are given in Tables I and II. Both authors used reduced copper as a catalyst for

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[12] Newitt, Byrne and Strong, *Proc. Roy. Soc. London*, **123A**, 236 (1929).

[12a] Since this was written, an article has appeared [Barnett F. Dodge, *Ind. Eng. Chem.*, **22**, 89 (1930)] in which it is argued that inaccuracy in the usually accepted value for the heat of formation of methanol may cause an error in the thermodynamically calculated K_p sufficient to account for the discrepancy.

studying Reaction II, and the analytical methods used by Lacy were essentially the same as those given by Christiansen, except that Lacy used a condenser at −80° which preceded two water and two sodium hydroxide scrubbers. In studying Reaction III Christiansen used a dynamic method with sodium methylate as a catalyst, whereas Lacy used a static method (autoclave plus pressure gage) with dissolved sodium methylate as a catalyst. Lacy started his experiments on Reaction III with mixtures containing 2 moles of $HCOOCH_3$, 8 moles of CH_3OH and 1 mole of CH_3ONa.

TABLE I

EQUILIBRIUM IN THE REACTION $2H_2 + HCOOCH_3 = 2CH_3OH$

$$K_p = \frac{(p_{HCOOCH_3})\ (p_{H_2})^2}{(p_{CH_3OH})^2}$$

Temp., °C.	K_p	Observer	Temp., °C.	K_p	Observer
(A) Hydrogenation					
198.9	0.059	C	197.6	0.068	C
199.6	.060	C	225	.148	C
198.7	.058	C	183.4	.041	C
224.8	.103	C	192.2	.056	C
227	.144	C	208.3	.090	C
			180	.030	L
(B) Dehydrogenation					
209	0.086	C	198.9	0.035	C
214.2	.105	C	200	.029	C
189.4	.048	C	200	.056	L
195.3	.050	C	200[a]	.052	L
231.2	.140	C	250	.018	L

[a] This second experiment at 200° was done at about one-third the space velocity of the previous determination.

TABLE II

EQUILIBRIUM IN THE REACTION $CH_3OH + CO = HCOOCH_3$

$$K'_p = \frac{(p_{CH_3OH})\ (p_{CO})}{(p_{HCOOCH_3})}$$

(A) Synthesis of $HCOOCH_3$			(B) Decomposition of $HCOOCH_3$					
Temp., °C.	K'_p	Observer	Temp., °C.	K_p	Observer	Temp., °C.	K_p	Observer
74	9.7	C	70	5.5	C	70	25	L
70	16.0	L	74	7.2	C	50	8.1	L
			102	2.2	C	30	2.3	L
			100	76	L			

The data of Tables I and II are plotted in Figs. 1 and 2, respectively, the common logarithm of the equilibrium constant being plotted against the reciprocal of the absolute temperature. Assuming that the slope of these curves remains constant up to 300°, we have for Reaction II the equation

$$\log K = -\frac{3149}{T} + 5.43 \qquad \text{(IV)}$$

and for Reaction III

$$\log K' = -\frac{1835}{T} + 6.6 \qquad \text{(V)}$$

In constructing Fig. 2, the curve as given favors Lacy's data rather than Christiansen's, for the latter are admittedly uncertain. Addition of Equations IV and V gives an equation for the equilibrium constant of Reaction I

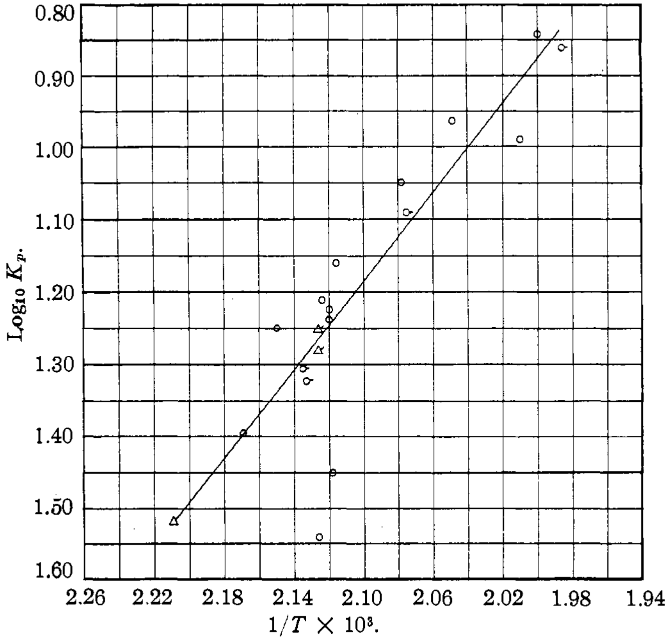

Fig. 1.—Reaction $2H_2 + HCOOCH_3 = 2CH_3OH$. ○, Hydrogenation, Christiansen; △, hydrogenation, Lacy. ○–, Dehydrogenation, Christiansen; △–, dehydrogenation, Lacy.

$$\log K'' = -\frac{4984}{T} + 12.04 \qquad \text{(VI)}$$

This formula yields the following equilibrium constants

Temp., °C.	200	250	300
$K''' = 1/K'' = (p_{CH_3OH})/(p_{CO})\,(p_{H_2})^2$	3×10^{-2}	3×10^{-3}	5×10^{-4}

These constants are of the same order of magnitude as those obtained by direct measurement (see Table VI).

Direct Measurement of Equilibrium in Reaction $2H_2 + CO = CH_3OH$

Description of Apparatus and Procedure.—The accompanying sketch illustrates the arrangement of the apparatus for the measurement of equilibrium from the decomposition side of Reaction I. Methanol was vaporized in a brass bomb (V) which was maintained at a constant temperature by the electric furnace (F) and the thermoregulator (R); 350 cc. of methanol was placed in the bomb, whose initial volume was 500 cc. The vapor pressure of the methanol was measured by a calibrated Bourdon gage.

A copper tube projecting from the bottom of the bomb into the vapor space was connected to the nipple (U). Through the tube and nipple the methanol vapor passed into the copper-lined bomb (B) containing the catalyst. The bomb was also maintained at a constant temperature by an electric furnace and a thermoregulator.

The off-gases passed through a copper tube to the pressure condenser (C). Methanol vapor was liquefied at this point and drawn off at the valve (X), while the non-condensable gases passed through the flowmeter (G) to the wetmeter (M). The space velocity of the gas was controlled by the valve (D) and was continuously indicated by the flowmeter.

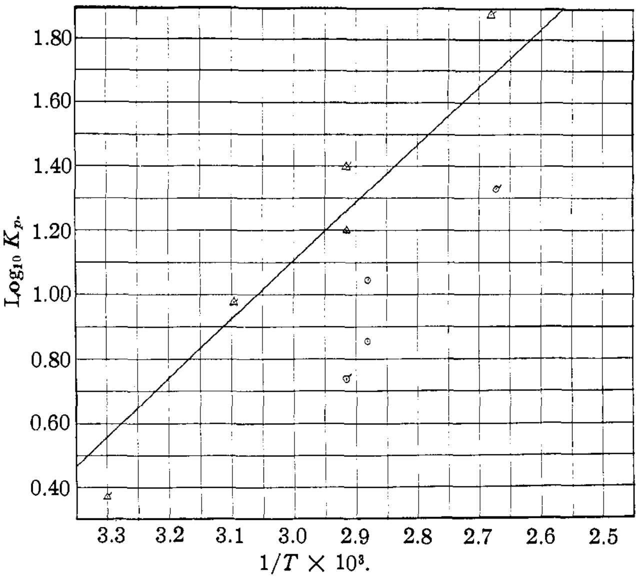

Fig. 2.—Reaction $CH_3OH + CO = HCOOCH_3$. ⊙, Christiansen, synthesis; △, Lacy, synthesis; ⊙–, decomposition; △–, decomposition.

For measurement of equilibrium in Reaction (I) from the synthesis side, the upper furnace and bomb were removed. Water gas which had been scrubbed with sodium hydroxide solution, then mixed with steam and passed over a water-gas shift catalyst at 450–500° and finally scrubbed again with sodium hydroxide solution, was compressed to the desired pressure, passed over activated carbon to remove any catalyst poisons and admitted to the catalyst chamber through the nipple (U).

Temperatures were measured by calibrated chromel–alumel thermocouples imbedded in the walls of the bombs. During a number of experiments on the synthesis side of Reaction I, an additional couple was imbedded in the catalyst itself. This consisted of a copper tube through which an insulated constantan wire had been thrust. The end of the tube was welded over the end of the constantan wire, forming the hot junction of a copper–constantan couple which was capable of withstanding several hundred atmospheres pressure and which exposed only copper to the reactants. No difference in temperature was observed between this internal couple and the external one in the wall of the bomb. The maximum error in reading the couples is estimated as ±2°.

During two experiments the off-gases were scrubbed in two bead towers containing water in order to determine the loss of methanol in the off-gases. The maximum error involved in neglecting this is less than 0.3%.

A few synthesis experiments were made at twenty atmospheres using the same type of apparatus with the exception of the condenser. The vapors and off-gases were expanded through a small needle valve directly into a glass condenser cooled by carbon dioxide snow mixed with methanol, the temperature inside the condenser coil being held between −75 and −80°.

In all of the experiments the catalyst employed was a mixture of the oxides of copper, uranium and thorium, supported on asbestos. This catalyst was prepared as follows: 83 g. of $Cu(NO_3)_2 \cdot 3H_2O$, 10 g. of $UO_2(NO_3)_2 \cdot 6H_2O$ and 5 g. of $Th(NO_3)_4 \cdot 12H_2O$ were dissolved in 500 cc. of water. Fifty grams of acid-washed asbestos fiber was mixed with the solution, which was then heated to boiling and 100 grams of potassium hydroxide dissolved in 250 cc. of water was added. The mixture was then filtered, the filter cake being washed free from nitrates, and then dried at 150°. Before use the catalyst was reduced at 150–200° by passing a mixture of 90% of hydrogen and 10% of methanol over it for several hours, the methanol being employed to avoid any sudden rise in temperature due to the heat of reduction of copper oxide.

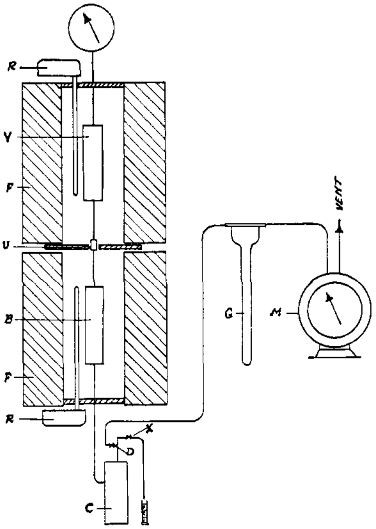

Fig. 3.—Apparatus for measuring equilibrium in the methanol reaction.

Results

Tables III, IV and V contain all of the essential data for the calculation of the equilibrium constants. Unless otherwise specified, the product was practically pure (above 95%) methanol, no correction being made for the small amounts of water, methyl formate and higher alcohols which were present. The method of calculation is as follows.

A = Off-gas in liters at 22° and 1 atmosphere
B = CH_3OH in liters at 22° and 1 atmosphere
C = $(A + B)$ = volume of equilibrium mixture calculated as at 22° and 1 atmosphere
D = $[(A + 3B) \times$ volume fraction of CO in entering gas $- B]$ = volume of CO in equilibrium mixture calculated at 22° and 1 atmosphere
E = $(A - D)$ = volume of H_2 in equilibrium mixture calculated at 22° and 1 atmosphere
P = total pressure

$$K_p = \frac{(p_{CH_3OH})}{(p_{CO})\,(p_{H_2})^2} = \frac{B \times C^2}{D \times E^2P^2}$$

The constant K_p was calculated using partial pressures as indicated above, no correction being made for the deviations of the gases from the laws of perfect gases, since so far as the pure substances H_2, CO and CH_3OH are concerned, such deviations are of the same order of magnitude as the experimental errors. The constants obtained by using fugacities are about 15% lower than those using pressures, whereas the average

TABLE III

EQUILIBRIUM DATA FOR SYNTHESIS OF METHANOL AT 50 ATMOSPHERES

Expt.	Off-gas, liters at 22° and 1 atm.	CH_3OH, cc. at 22°	CO in entering gases, %	Temp., °C.	S. V. H.	Conversion of CO to CH_3OH, %	K_p
7a	31.81	15.6	16.9	200	136	98.1	0.036
7b	35.74	17.6	16.9	200	48	98.3	.040
7c	28.67	14.1	16.9	200	90	98.3	.035
7d	28.16	46.4	27.5	200	63	88.0	.016
7e	31.72	53.8	27.5	200	75	91.2	.021
7f	35.71	10.2	16.6	250	83	69.4	.0014
7g	27.22	7.2	16.9	250	67	64.0	.0012
7h	35.32	9.4	18.1	250	75	60.0	.0010
8a	29.46	11.6	26.9	250	35	51.6	.0011
8b	30.90	12.8	27.5	250	35	52.0	.0011
8c	26.18	11.3	28.0	250	40	52.3	.0012
7i	74.29	6.2	19.3	300	90	22.7	.00019[b]
7j	77.54	6.0	19.3	300	60	21.3	.00017[b]
8d	52.75	4.8[a]	25.2	300	30	15.0	.00013
8e	42.61	3.9[a]	25.2	300	25	15.0	.00013
8f	33.28	2.6[a]	25.2	300	20	12.7	.00011
8g	48.40	3.6[a]	25.2	300	20	12.5	.00011

[a] This product was only 77% CH_3OH. In calculating the equilibrium constant the partial pressure of CH_3OH was taken as 77% of this pressure as ordinarily calculated, the partial pressures of CO and H_2 being calculated as indicated above (and hence no correction was made for the small amounts of CO and H_2 converted to products other than methanol).

[b] The average of these two values Nos. 7i and 7j, that is, $(0.00019 + 0.00017)/2 = 0.00018$, has been used in Table VI as the value for K_p at 300° from the synthesis measurements. The reason for picking out these values and discarding Nos. 8d, 8e, 8f and 8g is that the relatively low purity of the methanol produced in these last showed that, due to the much lower S. V. H., side reactions went onto a considerable extent, while in Nos. 7i and 7j this was not the case. Furthermore, since equilibrium is here being approached from the synthesis side, all observed values of K_p must necessarily be lower than the true value, consequently the higher figures represented by 7i and 7j should be nearer the true value of K_p.

TABLE IV

EQUILIBRIUM DATA FOR DECOMPOSITION OF METHANOL AT 50 ATMOSPHERES

Expt.	Off-gas, liters at 22° and 1 atm.	CH_3OH, cc. at 22°	Temp., °C.	S. V. H.	Decomposition, %	K_p
5a	26.54	11.6	250	90	55.8	0.0011
5b	32.54	17.2	250	85	50.0	.0015
5c	40.89	18.2	250	40	55.0	.0012
6a	28.66	3.0	300	90	84.0	.00019
6b	51.02	5.6	300	90	83.4	.00020
6c	32.21	3.3	300	55	84.3	.00019
6d	67.41	7.1	300	70	84.0	.00020

TABLE V

EQUILIBRIUM DATA FOR SYNTHESIS OF METHANOL AT 20 ATMOSPHERES

Expt.	Off-gas. liters at 22 °C. and 1 atm.	CH_3OH. cc. at 22°	Temp., °C.	CO in entering gas. %	S. V. H.	Conversion of CO to CH_3OH. %	K_p
3a	105.84	13.4	250	19.8	43	31.5	0.0019
3b	122.25	15.0	250	19.8	45	30.8	.0019
3c	96.22	11.0	250	19.8	27	28.9	.0017
3d	143.16	15.8	250	19.8	25	28.1	.0016

deviation from the mean of the pressure constants for the experiments at 50 atmospheres was 30% at 200°, 9% at 250° and 8% at 300°.

The space velocity per hour of the reactants (which will hereafter be designated as S. V. H.) was calculated as at one atmosphere and 22°. Hence in order to obtain the true S. V. H. inside the bomb, it is necessary to multiply by $T/(P \times 295)$, where T is the absolute temperature and P is the total pressure.

Discussion

Table VI contains the averages of the results of Tables III, IV and V, as well as the constants calculated for Reaction I via the methyl formate equilibria. This table also includes constants calculated by Kelley[2,3] and by Smith,[4] their equations being based on the use of the specific heat data of Parks[5] and of Kelley.[6] The experimental results of Smith and Branting[11] and of Newitt, Byrne and Strong,[12] and the results of calculations using the Nernst approximation formula are also included in Table VI.

TABLE VI

COMPARISON OF EQUILIBRIUM CONSTANTS OBTAINED BY VARIOUS METHODS

				Temperature. °C.				
No.	Method	Pressure. atm.	Reference	200 $K_p \times 10^2$	250 $K_p \times 10^3$		300 $K_p \times 10^4$	
1	Direct meas., synth. and decomp.	65–100	12	4.8[a]	2.1[a]		1.6	
2	Dir. meas., synth.	50	Authors	3.0	1.2	Av., 1.25	1.8	Av., 1.9
2a	Dir. meas., decomp.	50	Authors	...	1.3		1.95	
3	Dir. meas., synth.	20	Authors	...	1.8		...	
4	Dir. meas., synth.	1	11	...	...		6.5	
4a	Dir. meas., decomp.	1	11	...	...		6.5	
5	Via $HCOOCH_3$ reactions	1	Lacy, 1	3	3		5	
5a	Via $HCOOCH_3$ reactions	1	1	5	6		8	
6	Via third law calcd.	...	3	121	80		87	
7	Via Nernst approx.	...	Authors	8	4		4	

[a] By extrapolation of measurements at higher temperature.

The values of No. 1 of Table VI are those tabulated by Newitt, Byrne and Strong,[12] being derived from the general expression which they give to represent the results of all their measurements over the range 280–338°, namely

$$\Delta F = 70.5T - 30{,}500$$

which corresponds to

$$\log_{10} K_p = -15.42 + \frac{6672}{T}$$

The values of Nos. 4 and 4a were calculated from the results obtained by Smith and Branting[11] at 304°.

The Nernst approximation formula used to derive the data given in Table VI is

$$\log K = \frac{24{,}750}{4.58T} - 3.5 \log T - 3.2 \qquad \text{(VII)}$$

The chemical constants used in deriving Equation VII are: H_2 = 1.6, CO = 3.5, CH_3OH = 3.5, which correspond to the original conventional constants of Nernst.

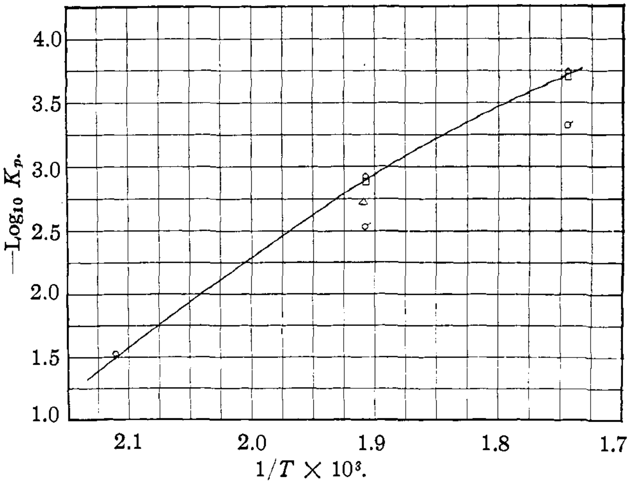

Fig. 4.—○, Synthesis at 50 atm.; △, synthesis at 20 atm.; □, decomposition at 50 atm.: Lacy, Dunning and Storch; ○-, via methyl formate reaction, Lacy and Christiansen.

The average values of Tables III, IV and V, *i. e.*, the values of Nos. 2, 2a and 3 of Table VI are plotted in Fig. 4, along with the data obtained from Lacy's and Christiansen's work. The slope of the curve gives for the heat of Reaction I, in the temperature range 200–300°, the value 24,000 calories. This is in fair agreement with the equation

$$\Delta H = -21{,}300 - 14.0T + 0.00825T^2 \qquad \text{(VIII)}$$

which is used by Kelley[2] and is based upon the following specific heat equations

$$H_2,\ C_p = 6.65 + 0.0007T \qquad \text{(IX)}$$

$$CO,\ C_p = 6.84 + 0.00038T \qquad \text{(X)}$$

$$CH_3OH_{(gas)},\ C_p = 6.16 + 0.0183T \qquad \text{(XI)}$$

and upon the following heat of formation of methanol

$$H_{(298)} \text{ for } 2H_2 + CO = CH_3OH_{(gas)} = -24{,}750 \text{ cal.} \qquad \text{(XII)}$$

Using Equation VIII and any point on the curve of Fig. 4, the following free energy equation for Reaction I is obtained

$$\Delta F = -21{,}300 + 14.0T \ln T - 0.00825T^2 - 30.84T \qquad \text{(XIII)}$$

An inspection of Table VI indicates that, excepting the calculations by way of the third law of thermodynamics, the constants are of the same order of magnitude. The third law calculations yield constants the lowest of which are 10–50 times larger than those determined experimentally. This very large discrepancy can scarcely be due to any large error in the experimental determinations, in view of the fact that the several experimenters agree as to the order of magnitude, nor can the discrepancy be attributed to any experimental error in the measurement of the specific heat of methanol, in view of Kelley's[6] recent work.

It is, however, conceivable that some constant error such as may for example be due to a very slow rate of approach to equilibrium of two forms of methanol may be involved. The value for the entropy of hydrogen used by Kelley[3] in calculating the entropy change of Reaction I is in error by an appreciable amount due to such a constant error, *viz*., the very slow rate of transformation of ortho to para hydrogen in the absence of a catalyst.[13,14]

It also appears desirable to review the experimental basis for the entropy of carbon monoxide, and to redetermine those values which involve a possible source of error.

The figure 1.6×10^{-4} obtained by Newitt, Byrne and Strong[12] for K_p at 300° agrees fairly well with the average value of the authors' constant for the same temperature (which rests on measurements made at 50 atm., *i. e.*, in the same pressure range), namely, 1.9×10^{-4}. (A difference in temperature of about 3° would account for this small difference in K_p). This value of K_p for 300°, however, differs quite considerably from Smith and Branting's average value of 6.5×10^{-4}, which rests on measurements made at atmospheric pressure.

This 4:1 discrepancy cannot be due to errors introduced by the use of pressures instead of fugacities,[15] for such errors would decrease by about 15% the constants obtained by the authors and by Newitt, Byrne and Strong, thus increasing the difference between these results and those of Smith and Branting. Two other possible explanations of this discrepancy are: first, the possibility of solvent effects in the gas mixture causing the fugacities of the constituents to be different from what they would be in an ideal solution; second, experimental errors.

Smith and Branting's equilibrium determinations at atmospheric pressure can hardly be in error due to solvent effects, since these are usually

[13] Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929).

[14] Rodebush, *Proc. Nat. Acad. Sci.*, **15**, 678 (1929).

[15] For pressure–fugacity relations, see Fig. 4 of Smith and Branting's article.

negligible at atmospheric pressure.[16] If the solvent effect which was calculated for ethylene–argon mixtures under pressure at 25° by Gibson and Sosnick[16] also exists in mixtures of methanol, hydrogen and carbon monoxide, then it is quite possible that the equilibrium constants obtained at 50–70 atmospheres may be in error by a few per cent. Whether this error would make the constants obtained at 50–70 atmospheres larger or smaller than those obtained at one atmosphere is uncertain, but it seems unlikely (although not impossible) that the solvent effect will explain a discrepancy as large as 300–400% such as exists between the determinations made at 50–70 atmospheres pressure and those made at one atmosphere, for deviations from the laws of perfect solutions of sufficient magnitude to account for such large errors have never been reported. In fact, in the closely parallel case of nitrogen and ammonia, studied by Lurie and Gillespie[17] for a temperature of 45° and total pressures of 7 to 60 atmospheres, the data indicate no deviation whatever from the laws of ideal solutions. Similarly in the work of Larson and Dodge[18] on equilibrium in mixtures of nitrogen, hydrogen and ammonia, the differences between the constants obtained at 50 atmospheres and at one atmosphere are practically negligible, being about 2% at 500°, 6% at 450°, 1% at 400°, 3% at 375° and 6% at 350°. These differences are so small and irregular that experimental error will probably account for them.

It seems more probable that the discrepancy between the constants obtained at one atmosphere and those obtained at 50–70 atmospheres is due to experimental errors. The fact that the two entirely distinct series of high pressure equilibrium determinations, one made by Newitt, Byrne and Strong and the other by the authors, give closely concordant results, makes any serious experimental error in the value of the constant for 300° and 50–70 atmospheres seem highly improbable. Concerning the possibility of experimental error in Smith and Branting's measurements at one atmosphere, despite the great care which they exercised in establishing the validity of their analytical methods and data, the fact must be considered that difficulties of experimental technique in any determination at one atmosphere are very great. Thus while in the authors' work at 50 atmospheres the methanol constituted about one-tenth of the equilibrium mixture, and the amounts of methanol separated were of the order of 5 to 20 g. (thus permitting fractional distillation, boiling point and density determinations), in Smith and Branting's work the methanol made up only 1/10,000 of the equilibrium mixture, and the amount of methanol (estimated colorimetrically) apparently obtained in a week's run was only about 0.003 g. The possibility of serious error in estimating

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[16] Gibson and Sosnick, THIS JOURNAL, **49**, 2172 (1927).

[17] Lurie and Gillespie, *ibid.*, **49**, 1146 (1927).

[18] Larson and Dodge, *ibid.*, **45**, 2918 (1923).

such minute quantities of methanol is apparent if one considers the chance of the presence in the catalyst or in the original CO + H_2 mixture of a minute amount of some volatile organic impurity not decomposable by the catalyst and reacting like methanol in colorimetric tests. Smith and Branting do not state whether blank tests to eliminate such possibilities were made, for example, blank tests consisting of passing the CO + H_2 mixture through a reaction vessel not containing any catalyst, and of passing hydrogen alone through the catalyst.

Summing up the conclusions as to this 4:1 discrepancy: the explanation consists either in experimental error in the determination at one atmosphere, or in the value of the constant for 50–70 atmospheres being, in fact, only about one-fourth of the value of the constant for one atmosphere as a result of a very large solvent effect (according to which the fugacities of methanol, and perhaps also those of hydrogen and of carbon monoxide or of all three, in mixtures of these at 50–70 atmospheres deviate enormously from the fugacities of these constituents in the pure state. In fact, the pressure range might be given as 20–70 atmospheres, in which the constants are only about one-fourth of those at one atmosphere, in view of the fair agreement between the synthesis figures at 20 atmospheres and the 50 atmospheres pressure data summarized in Table VI.

In view of the above considerations, it appears very desirable to carry on further determinations at one atmosphere, and to extend the range of the equilibrium determinations to pressures of 5, 10 and 20 atmospheres. Such additional experimental data would not only furnish information concerning the variation of the equilibrium constant with pressure, but would also present additional evidence as to whether the deviations of gaseous mixtures from the laws of perfect solutions can really be large enough to account for a 4:1 variation in equilibrium constants in so moderate a range of pressure as 1 to 50 atmospheres.

For 250° it will be noted that the value for K_p obtained by the authors in direct measurements at this temperature (at 50 atm.), namely, 1.25×10^{-3}, differs appreciably from the value of 2.1×10^{-3} which is calculated by Newitt, Byrne and Strong by extrapolation of their measurements made between 280 and 338° at pressures of 65 to 100 atmospheres.

Summary

The equilibrium constants for the reaction $2H_2 + CO = CH_3OH$ were measured from both the synthesis and decomposition sides at 250 and 300°, and also at 200° from the synthesis side only, using in all cases 50 atmospheres total pressure. Some measurements were also made from the synthesis side at 250° using 20 atmospheres total pressure.

These equilibrium constants were also calculated from measurements of equilibria in the two reactions.

$$2H_2 + HCOOCH_3 = 2CH_3OH$$
$$CH_3OH + CO = HCOOCH_3$$

Both sets of constants are of the same order of magnitude (they agree within a factor of about three), but the lowest figures obtained by calculations based on the use of specific heat data, and the estimated entropies of hydrogen and oxygen, are about 10–50 times as large as those obtained experimentally. The existence of a large discrepancy here, which was mentioned by Smith and Branting, is thus confirmed.

The data obtained by the authors at 300° and 50 atmospheres pressure agree very well with those obtained at 70 atmospheres by Newitt, Byrne and Strong, but are only about three-tenths as large as those obtained by Smith and Branting at atmospheric pressure. A discussion of possible explanations of this discrepancy is presented.

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THE NEPHELOMETRIC ANALYSIS OF ZINC

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RECEIVED OCTOBER 16, 1929 PUBLISHED MARCH 6, 1930

In plant and animal tissues certain elements occur in amounts that are too small for accurate determination by the usual methods of quantitative analysis and yet comparatively gross for application of the methods of microchemistry. Zinc, which is one of these elements, is apparently important to animal life. Its wide distribution in food—particularly its concentration in the germ elements, such as the endosperm of grain and yolk of egg—points to a possible need. Furthermore, tissue zinc is susceptible to changes in condition which affect the salt metabolism in general[1] and which indicate some function as yet unknown in cellular processes.

Unfortunately, methods for the analysis of the small amounts of zinc that occur in animal tissues and fluids are difficult, and results approaching exactness are attained only with considerable skill and experience. This is owing not only to the fact that these traces of zinc are found in the presence of enormously greater quantities of other salts, but more particularly to the fact that zinc forms no useful colored salts, nor very insoluble compounds which sharply differentiate it from its milieu.

No simple, exact method for the gross estimation of zinc has yet been found in spite of the expenditure of considerable effort in this direction.[2] Methods for the analysis of *traces* of the metal are quite as unsatisfactory. Of the methods available for the analysis of amounts of zinc in the vicinity of

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[1] L. T. Fairhall, *J. Biol. Chem.*, **70**, 495 (1926).

[2] F. R. Bichowsky, *J. Ind. Eng. Chem.*, **9**, 668 (1917).