Eastman's data (*2*) give the equilibrium constant for the water-gas reaction as 34 at 304° C. It is interesting to note how closely equilibrium is apparently reached in this reaction.

Lack of time prevented further investigation of these reactions and use of other catalysts. However, most methanol catalysts of which we have knowledge produce carbon dioxide or water or both with methanol. An investigation similar to the present one at high pressures with accurate determination of water and carbon dioxide partial pressures at equilibrium would be of interest. It is possible that the mechanism of formation of methanol from hydrogen and carbon monoxide may not be so simple as indicated by Equation 1, especially as a steady state is approached.

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The Methanol Equilibrium[1,2]

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In spite of all the published work on this subject there are still some striking discrepancies to be cleared up. Previous workers have attacked the problem from three angles: (1) calculation of the equilibrium constant, K_p, via the third law of thermodynamics making use of absolute entropies or by means of the Nernst approximation; (2) indirect measurement of K_p by experimental study of equilibrium for reactions whose combination yields the methanol synthesis reaction; and (3) direct determination of K_p for the methanol reaction at atmospheric and higher pressures.

The experimental investigations agree only as to order of magnitude, the disagreement being as much as several hundred per cent. Only a small part of this discrepancy can be accounted for by the effect of pressure on K_p. This is treated in detail in the paper and values of K_{p_0} (equilibrium constant at low pressures, where gases are substantially ideal) are calculated with the aid of van der Waals' equation. The equilibrium constants calculated via the third law are anywhere from 12 to 1500 times the experimental ones. It is believed that a large part of this difference is due to inaccuracies in the thermal data, though this has been disputed by others.

Some new experimental data obtained by the direct method at 170 atmospheres and temperatures ranging from 260° to 310° C. are presented. These data must be regarded as preliminary, but it is believed that they represent an improvement over the previous data obtained at pressures higher than atmospheric. The constants agree fairly well, at the lower temperatures, with those obtained in the one published investigation by the direct method at 1 atmosphere and are considerably higher than those obtained in two investigations at higher pressures.

The results of previous investigations are critically compared with these new data and various sources of error in the experimental determination of K_p's and their interpolation and extrapolation by means of thermal data are discussed. The influence of side reactions on the experimental measurements is particularly stressed. The new data still leave an enormous gap between experimental and calculated results.

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IN SPITE of the many recent papers on this subject, there still exists considerable uncertainty as to the exact position of the equilibrium in the reaction:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (1)$$

Results of the various experimental investigations are quite conflicting. Equilibrium constants calculated from thermal data are scarcely of the same order of magnitude as those obtained experimentally. The need for more work is obvious, especially in view of the fact that this reaction is of great importance both industrially and scientifically. It is particularly important to establish the reasons for the great difference between calculated and experimental results, because many such calculations are now being made and we can have but little confidence in them when we fail to get even order-of-magnitude agreement in a test case where the data are probably better than the average.

It is the purpose of this paper to review the work on this subject and to present some new experimental results, of a preliminary nature, obtained at a pressure of 170 atmospheres.

Previous Work

There have been three main avenues of attack on this problem:

(1) Calculation by means of the Nernst approximation formula or by the third law of thermodynamics.

(2) Indirect measurement involving the reactions

$$2H_2 + HCOOCH_3 \rightleftharpoons 2CH_3OH \qquad (2)$$

$$CH_3OH + CO \rightleftharpoons HCOOCH_3 \qquad (3)$$

or the reactions

$$H_2 + CO \rightleftharpoons HCOH \qquad (4)$$

$$HCOH + H_2 \rightleftharpoons CH_3OH \qquad (5)$$

(3) Direct measurements on Reaction 1.

Matignon (*16*), Audibert and Raineau (*1*), and Brown and Galloway (*3*) have calculated K_p for Reaction 1 by means of the Nernst approximation formula. Kelley (*11*), Smith (*18*), Francis (*8*), and Dodge (*6*) have attempted to calculate $\Delta F°$ and, hence, K_p for Reaction 1 with the aid of absolute entropies and the third law of thermodynamics. Ghosh and Chakravarty (*9*), Christiansen (*5*), and Lacy, Dunning, and Storch (*13*) used the indirect method, the first mentioned pair of investigators making use of Reactions 4 and 5 and the others of Reactions 2 and 3.

Direct equilibrium measurements on Reaction 1 have been published by Smith and Branting (*19*), Newitt, Byrne, and

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[2] Taken in part from a dissertation presented by Mr. von Wettberg to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of doctor of philosophy, June, 1930.

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Strong (*17*), and Lacy, Dunning, and Storch (*13*). Audibert and Raineau (*1*), Lewis and Frolich (*14*), and Brown and Galloway (*3*) have measured the percentage of carbon monoxide converted to methanol by Reaction 1 at low space velocities in connection with catalyst investigations. Although these measurements were not made primarily for the purpose of determining the equilibrium, nevertheless they should give results approximating equilibrium conditions, and are properly classed with the direct equilibrium measurements. Fieldner and Brown (*7*) have summarized the work of these last three pairs of investigators.

In Table I there are presented some typical results by various investigators. Results calculated via the Nernst approximation formula are not included, as this formula has little scientific foundation and the results could not be expected to be more than order of magnitude. The most outstanding discrepancy is that between the calculated results and those obtained from experimental measurements. Even the calculated results do not agree very well among themselves. The reasons why accurate results can hardly be expected from the third-law calculations have been discussed in a recent paper (*6*) by one of the authors. Smith and Hirst (*20*) have, however, taken exception to the conclusions reached in this paper. They also pointed out a numerical error, which is hereby acknowledged but which does not seem to the authors to invalidate the general conclusions reached. The experimental measurements with one exception agree as to order of magnitude, but the problem can hardly be regarded as solved when differences of several hundred per cent in the experimental values of K_p still exist. Curiously enough, the one exception consists of results that agree as to order of magnitude with the third-law calculations, but a critical study of the paper convinced the present writers that these results cannot be given much weight.

It is recognized that part of the differences shown in Table I are due to the fact that the results are not all for the same pressure, and K_p is known to be a function of pressure. The calculated results, being based on standard free-energy changes, give directly K_p for a standard state of pressure which, in Lewis' (*15*) system of thermodynamics is practically 1 atmosphere. It should also be noted that K_p is a function of the composition of the equilibrium mixture at a given pressure and temperature. It is believed that neither of these effects is sufficient to account even for the discrepancies between the various experimental K_p's. This point will be taken up later. Finally, it should be noted that some of the differences exhibited in Table I are due to the use by the various investigators of different thermal data to interpolate and extrapolate their experimental results.

Apparatus and Experimental Procedure

Equilibrium was approached from both sides, using a dynamic method whose general features may best be explained with reference to Figure 1. Carbon monoxide was generated by the dehydration of formic acid over phosphoric acid and mixed in approximately the stoichiometric proportions with commercial electrolytic hydrogen that had been deoxidized over a copper catalyst. The mixture was scrubbed with caustic soda solution and then compressed to the four cylinders shown, two being used to maintain a constant pressure supply of gas to the reactor and the other two used as auxiliary storage. From the storage system the gas passed through the purifying tower, *F*, containing activated silica gel. Beyond this tower the system up to the catalyst was essentially non-ferrous in order to eliminate the possibility of trouble from iron carbonyl. After this final purification the gas passed to the saturator, *J*, where it bubbled through methanol. The saturator, shown in greater detail in Figure 2, was constructed from bronze hexagon stock and provided with suitable head for gas and liquid connections. It was surrounded by a motor-stirred oil bath which was electrically heated by means of an immersion heater and a nichrome ribbon winding on the outside of the container. The oil bath was well insulated thermally and its temperature automatically controlled by a bimetallic thermostat. The maximum possible methanol pressure that can be produced is, of course, the critical pressure of 78.7 atmospheres. The mol per cent of methanol in the saturated gas is approximately double that calculated from the vapor pressure, assuming ideal gases. The saturator was calibrated at several temperatures by passing the storage gas mixture through it at 170 atmospheres, expanding the gas to 1 atmosphere, and condensing the methanol at the temperature of solid carbon dioxide. A calibration curve was constructed from which the mol per cent of methanol in the gas at any temperature could be read. From the saturator the gas passed through an electrically heated tube to the catalyst reactor, *L*. The reactor, shown in greater detail in Figure 3, was constructed from a chrome-vanadium steel tube, *A*, fitted with copper liner, *D*. Head *B*, carrying thermocouple well, *F*, and gas exit connection was welded to the alloy steel tube. The bottom of the reactor was closed by the nipple, *E*, held by nut *C* against a confined copper gasket. The gas inlet and outlet connections were made by means of 60-degree cones on the ends of the copper-lined steel tubing. (U. S. Dept. Agriculture, *Circ.* **61.**) The thermocouple well was held in place by a cone-type compression union.

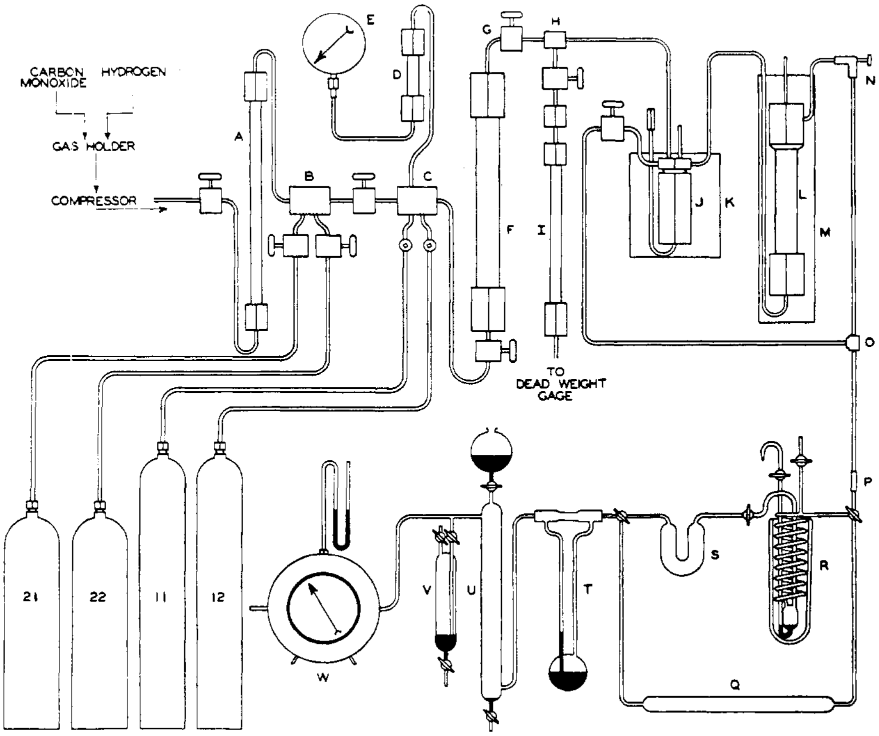

Figure 1—Diagram of Equilibrium Apparatus

For temperature control the reactor was immersed in a lead-antimony bath contained in the steel pipe, *H*, which was wound with nichrome ribbon for heating and thermally insulated with 85 per cent magnesia. The ribbon was insulated from the metal by four thicknesses of asbestos paper. Suitable means were provided for holding the reactor in the bath against the buoyant force of the lead. Considerable trouble was experienced from lead working into the joints and loosening the heads and tubing connections. The loosening did not seem to occur as long as the lead was kept molten, but only when it was allowed to solidify and then remelted. The difficulty was largely overcome by coating all joints with a liberal application of a mixture of talc and Meprolene oil to keep out the lead and also by maintaining the lead molten for long periods.

Table I—Values of K_p Obtained by Previous Investigators

Pressure Atm.	$K_p \times 10^3$ at 250° C.	$K_p \times 10^4$ at 300° C.	$K_p \times 10^5$ at 350° C.	$K_p \times 10^6$ at 400° C.	Method of Investigator
...	74	81	140	280	Calcd. by third law (*11*)
...	1300	800	1200	2500	Calcd. by third law (*18*)
...	1300	1400	2200	4500	Calcd. by third law (*8*)
1.0	320	430			Indirect method using Reactions 4 and 5; K_p calcd. from their equations (*9*)
1.0	4.7	6.0			Indirect method using Reactions 2 and 3; K_p calcd. from his equation (*5*)
1.0	3.1	4.5			Indirect method using Reactions 2 and 3; K_p calcd. from his equation (*13*)
50	1.25	1.90			Direct method, both synthesis and decomposition (*13*)
1.0	5.90	6.40	7.90	20	Direct method, both synthesis and decomposition; K_p calcd. from their equation (*19*)
70–100	2.1	1.6	2.0	3.1	Direct method, both synthesis and decomposition; K_p calcd. from their equation (*17*)
204				18.0	Direct method, from synthesis side only (*14*)
150				19.2	Direct method, from synthesis side only (*1*)
180				19.8	Direct method, from synthesis side only (*3*)

From the reactor the gas was expanded to atmospheric pressure by valve *N*, and conveyed through electrically heated tubing to the glass analytical train. Methanol and other condensable vapors were removed in the coil, *R*, immersed in carbon dioxide snow and alcohol. Any residual vapor was caught in the silica gel tube, *S*. Later two condensers were used and the gel tube was eliminated. The methanol-free gases were passed through flowmeter *T* to control the space velocity, saturated with water in *U*, sampled over mercury in *V*, and measured by the calibrated wet gas meter, *W*. *Q* was a silica gel tube in a by-pass line used only during the period directly preceding a run.

Pressure was measured by a dead-weight piston gage. The constant operating pressure was maintained on the gas in cylinder 22 by bleeding gas from 21, where it was stored at a higher pressure, the bleeding being manually controlled on the basis of the piston gage indications. This control was simple and variations easily held to less than 0.5 atmosphere. Temperatures in the lead bath and in the catalyst bed were measured by chromel-X-copel couples and Leeds and Northrup portable indicating potentiometers. Variations of 1.0° C. were about the smallest that could be detected with certainty. The temperature of the lead bath was readily controlled manually, so that its temperature variation was no more than the limit of temperature variation that could be detected. The thermocouple well, *F* (Figure 3), could be varied in position and was placed so that it projected only a short distance into the catalyst bed near the gas exit end. Temperatures measured by this couple were consistently higher than the temperature measured in the bath. The differences between the two varied between different runs, but was very constant during any given run. In the majority of runs the difference was less than 3° C., but in some cases was greater, the extreme difference being 12° C. Owing to the exothermal character of the reaction, conduction along thermocouple well, and relatively low rate of heat transfer from a fluid moving at such a low velocity, it is not easy to obtain a reliable temperature measurement. If any error existed, the temperatures are believed to be low rather than high.

The reactor was filled with about 60 cc. of 8- to 14-mesh catalyst granules. In runs 8 to 12, inclusive, a zinc-chromium catalyst was used, and in the remainder of the runs a zinc-copper catalyst was used. Each run was preceded by a warming-up period long enough so that the gas in the catalyst space was completely changed at least once. During this period all instruments were read to give an indication of the attainment of constant conditions, but no measurements recorded as final data. The condenser, *R*, was by-passed and the gas sent through *Q* during this time. At the conclusion of the run the liquid condensate was blown from the condenser into a previously chilled receiver and tightly stoppered. The condenser was then rinsed out with small portions of water. When the gel tube, *S*, was used, its adsorbed liquid was removed by steaming.

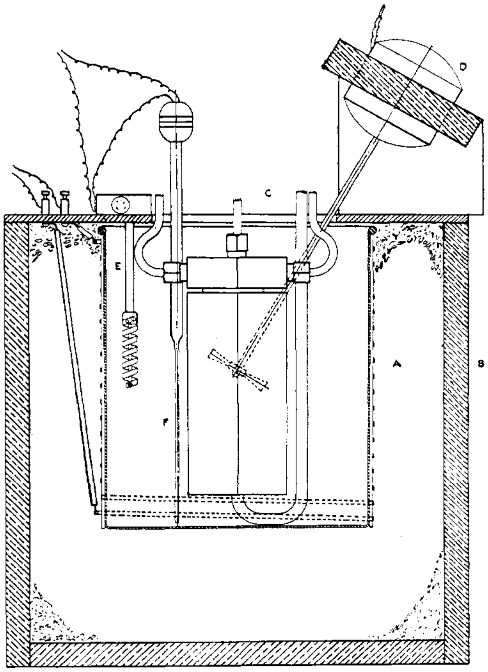

Figure 2—Methanol Saturator

Various methods were tried for the determination of the methanol in the condensate. Estimation by gravity or refractive index is open to the objection that these methods cannot be accurate unless water is the only condensable byproduct, which may be far from true. Considerable experimenting was done on the colorimetric method developed by Smith and Branting (*19*) from the well-known formaldehyde tests using Schiff's reagent. In spite of their statement to the contrary, the present writers have proved beyond a doubt that dimethyl ether does interfere in this test. Since dimethyl ether was shown to be present in many of the runs, this method was abandoned. Rectification was finally adopted as the most satisfactory method of determining methanol. The condensate (from 14 to 40 cc. were available from a run) was distilled through a Hempel column and, by using at the start a reflux condenser with cooling medium at about −25° C., dimethyl ether and methanol could both be determined with reasonable accuracy.

The storage gas was substantially a 2-to-1 hydrogen-carbon monoxide gas containing a small percentage of inerts. Its exact composition varied somewhat and no attempt was made to determine it for each run. The gases leaving the catalyst were, however, sampled continuously during the run and carefully analyzed using a modified Orsat apparatus equipped with mercury-filled, compensated buret.

Data and Calculations

Twenty-seven runs were made, but data for only fourteen of them are presented in this paper. The results calculated from the data taken in these runs are shown in Table II. It should be emphasized that these data are preliminary and are presented largely to bring out more clearly than has been done in the past some of the serious obstacles in the way of determining accurately the equilibrium in a reaction of this type. Certain of the data are believed to be more reliable than previously published data obtained in the study of this reaction under pressure. Table III gives the analyses of off-gas and methanol content of the condensate.

Table II—Summary of Equilibrium Data

Run	Temp.	Off-Gas[a]	Space Velocity[b]	MeOH in Entering Gas	H_2 Off-Gases	CO Off-Gases	MeOH Off-Gases	$K_p \times 10^4$	$K_{p_0} \times 10^4$
	° C.	Liters		Mol %	Mol %	Mol %	Mol %		
8	329	60.0	1040	None	57.90	12.68	16.95	1.40	0.71
9A	300	36.2	1208	None	55.20	14.45	22.35	1.80	0.85
$9B_1$	302	19.5	309	None	53.40	8.32	22.10	3.20	1.45
$9B_2$	301.5	24.2	301	None	55.10	8.05	21.20	3.00	1.43
10	309	41.1	1110	None	60.90	13.50	21.30	1.50	0.73
12	302	28.5	273	30.5	44.90	9.47	23.70	4.30	1.94
15	258.5	6.39	547	47.5	17.80	6.07	71.70	129.0	48.3
16	259	6.36	221	0	21.90	5.70	66.50	84.0	31.0
17	274	9.78	224	40.0	26.90	7.30	56.10	37.0	15.0
18	273	5.41	114	40.0	28.70	7.80	53.00	29.0	11.8
19	307	17.1	259	25.5	46.60	8.65	23.30	4.30	1.96
20	307	14.35	248	40.5	43.30	9.04	25.00	4.6	2.10
22	258	7.97	500	47.0	18.90	8.14	70.40	84.0	31.4
23	298	27.0	575	16.5	34.40	11.20	42.40	11.0	5.20

[a] Dry and at standard conditions.
[b] Liters of total off-gas per hour per liter of catalyst.

Table III—Analytical Data

Run	Gas Analyses							Analysis of Condensate[a]	
	CO_2	Ill.	O_2	CO	CH_4	H_2	N_2	MeOH	Me_2O
	%	%	%	%	%	%	%	% by wt.	
8	6.0	0.1	0.4	16.2	0.6	74.1	2.6	83	12
9A	2.6	0.1	0.5	19.3	0.4	73.8	3.3	89	8.2
$9B_1$	6.0	0.1	0.6	11.8	0.5	75.7	5.3	74.5	18.2
$9B_2$	6.4	0.1	0.7	11.2	0.4	76.7	4.5	76	17.5
10	3.9	0.1	0.5	18.0	0.4	73.9	3.2	85	11.7
12	13.3	0.6	0.2	14.2	2.0	67.4	2.3	71	21
15	2.6	0.2	1.2	21.4	1.9	70.8	1.9	100	None
16	3.4	0.3	0.5	17.1	2.7	65.4	10.6	103	None
17	8.3	0.3	0.6	17.6	3.8	64.9	4.5	95	None
18	10.8	0.5	0.7	14.7	4.9	64.7	3.7	95	None
19	11.4	0.3	0.8	12.1	6.6	65.4	3.4	84	None
20	14.3	0.2	0.4	13.1	7.3	62.8	1.9	86	None
22	2.1	0.2	0.7	27.4	1.7	63.2	4.7	100	None
23	6.3	0.9	0.8	21.0	2.9	64.5	3.6	93	None

[a] Assuming it to consist only of methanol, methyl ether, and water.

The equilibrium constant, K_p, was calculated from the following expression:

$$K_p = \frac{Px_{\mathrm{MeOH}}}{(Px_{\mathrm{H_2}})^2 \times (Px_{\mathrm{CO}})} \qquad (6)$$

P = total gas pressure
x = mol fraction in equilibrium mixture

In getting the mol fractions of the three gases at equilibrium the total number of mols of gas present are needed. Certain assumptions were made in arriving at this figure for each run. An amount of water vapor equivalent to the methyl ether was assumed to be present in the runs with zinc-chromium catalysts. In the later runs, although there was no ether, there appeared to be small amounts of water and higher alcohols, which were estimated from the total weight of condensate and the distillation curves. The effect of these assumptions is to make only a small correction. The question as to the side from which equilibrium was approached in a given run is not always easy to decide. In case of a run like No. 20, where the mol per cent of methanol in the entering gases is much greater than in the off-gases, there appears to be no doubt that the equilibrium was approached from the decomposition side. In cases like run 19 one cannot be certain. Runs 12 and 20 are the only ones in which equilibrium was certainly approached from the decomposition side.

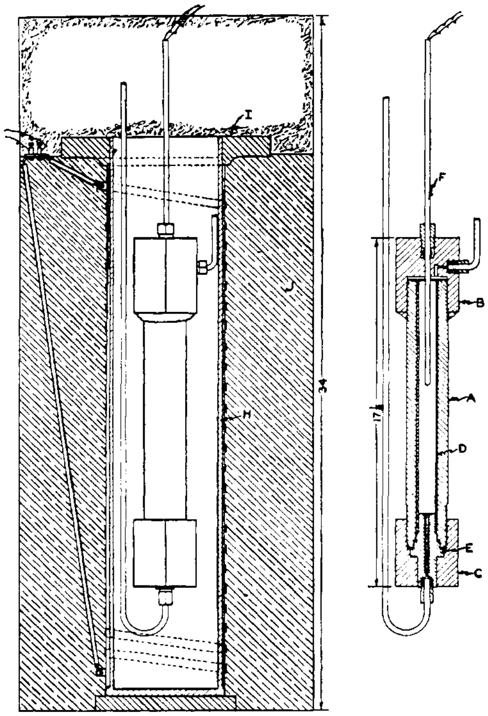

Figure 3—Equilibrium Reactor and Lead Bath

Discussion of Results

In attempting to compare the results of different investigators on the methanol equilibrium, one is immediately confronted with the difficulty that the equilibrium constant as ordinarily defined and as it is defined above is a function of the pressure. The values of K_p calculated with the aid of the third law are obtained from "standard" free-energy values by means of the well-known relation

$$\Delta F^\circ = -RT \ln K_p$$

The standard reference state for gases usually chosen, following Lewis and Randall (*15*), is one for which the fugacity is unity and the properties are those for a gas at infinite dilution. This is a purely hypothetical standard, but for all practical purposes is equivalent to choosing 1 atmosphere as the standard pressure. Thus, we have values of K_p for the methanol reaction at various pressures from 1 to 200 atmospheres and, to be comparable, they should be reduced to a common pressure. Furthermore, they are not strictly comparable unless the composition is the same at a given temperature and pressure. This latter effect will be neglected for the present.

Detailed treatment of equilibria for the general case—that is, without the assumption of ideal solutions—was given many years ago by van der Waals, based on the work of Gibbs, and is summarized in the text by van der Waals and Kohnstamm (*21*). Another treatment, the same in principle but differing in detail, is that of Lewis (*15*), involving the use of the special functions fugacity and activity. Still more recent treatments have been published by Gillespie (*10*), Keyes (*12*), and Beattie (*2*), the latter giving the most completely developed and comprehensive treatment yet published for the particular case of chemical equilibrium in non-ideal systems.

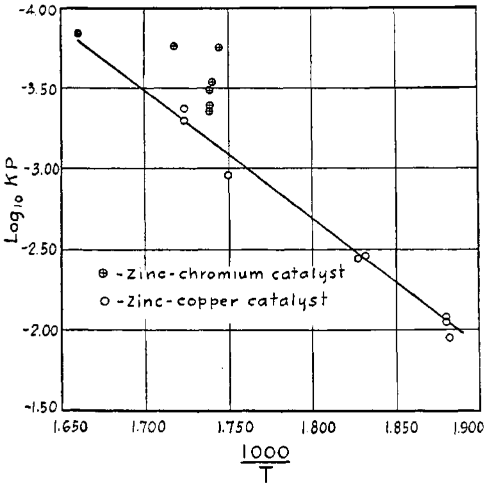

Figure 4—Log$_{10}$ K_p Versus 1000/T

Making use of the Gibbs chemical potentials (partial molal free energies in the Lewis system) and following in general the treatment of van der Waals and his pupils, one may write the general mass-action law for the reaction $aA + bB \rightleftharpoons cC$ as follows:

$$\frac{[x_C e^{\phi_C}]^c}{[x_A e^{\phi_A}]^a [x_B e^{\phi_B}]^b} = e^{-\frac{\Sigma\nu F'}{RT} - \Sigma\nu \ln p'} \tag{7}$$

where x_A, x_B, and x_C are equilibrium mol fractions of the three reacting species and e is the base of natural logs.

$\Sigma\nu F' = cF'_C - aF'_A - bF'_B$ (same as $\Delta F°$ in the Lewis system)

F'_A, etc., are the thermodynamic potentials or free energies of components A, etc., at the temperature in question and at some initial, arbitrary, standard pressure, p'.

R is the gas constant.

$$\phi_A = \pi - x_B\left(\frac{\partial\pi}{\partial x_B}\right) - x_C\left(\frac{\partial\pi}{\partial x_C}\right)$$

$$\phi_B = \pi + (1 - x_B)\left(\frac{\partial\pi}{\partial x_B}\right) - x_C\left(\frac{\partial\pi}{\partial x_C}\right)$$

$$\phi_C = \pi + (1 - x_C)\left(\frac{\partial\pi}{\partial x_C}\right) - x_B\left(\frac{\partial\pi}{\partial x_B}\right)$$

$$\text{and } \pi = \frac{\int v\,dp}{RT}$$

Choosing 1 atmosphere for the standard pressure, p', the expression on the right-hand side of Equation 7 reduces to $e^{-\frac{\Sigma\nu F'}{RT}}$. This is an equilibrium constant which is a function of temperature, but independent of the pressure or composition, and will be represented by K_{p_0}. Comparing this constant with K_p as expressed by Equation 6, it is clear that K_p must depend on both pressure and composition. It can readily be shown that $x_A\, e^{\phi_A}$ is identical with Lewis' $\bar{f}_A$, the "partial fugacity" of component A in the solution, and similarly for the expressions involving B and C. The application of Equation 7 to obtain numerical values of K_{p_0} requires a knowledge of the compressibilities of the gaseous solutions of the three components over the pressure and temperature range to be covered, or, better still, an equation of state for mixtures of these components, valid over the desired range. Such data are not available for the system under consideration. Beattie (*2*) has given the complete solution in terms of his own equation of state, but the constants of his equation of state for methanol are not known, and his method of getting the constants of the equation for the mixtures from those of the pure components is not well established.

Assuming the equilibrium mixture to be a solution of ideal gases, Equation 7 at once reduces to the familiar mass-action law for ideal gases, since for this case $\pi = \ln p$ and $\left(\frac{\partial\pi}{\partial x}\right) = 0$. Since, under the experimental conditions chosen, methanol is in the neighborhood of its critical state, the deviations from ideal behavior must be very large. Probably the best assumption that can be made at present is that each gas in the mixture behaves as if it were alone at the given temperature and at the total pressure of the mixture. This is the same as using for each gas its own equation of state, which would be valid if it were the only gas present. Such an assumption cannot possibly be true. Nevertheless, it may be a much closer approximation to the truth than the assumption of ideal gases. Mathematically, this is equivalent to assuming that π is not a function of x or that $\left(\frac{\partial\pi}{\partial x}\right) = 0$. Making this assumption, Equation 7 reduces to:

$$\frac{[x_C\, e^{\pi_C}]^c}{[x_A\, e^{\pi_A}]^a\, [x_B\, e^{\pi_B}]^b} = K_{p_0} \tag{8}$$

This assumption is the same as that involved in the fugacity rule of Lewis and Randall (*15*, p. 226), which has been used by various investigators (*3*, *19*, *10*), to aid in interpreting high-pressure equilibrium data. This simple interpretation of the rule has not been published before to the writers' knowledge. Thus, if, as given above, $\bar{f}_A = x_A\, e^{\phi_A}$, then $\bar{f}_A = x_A\, e^{\pi_A}$, when $\left(\frac{\partial\pi}{\partial x}\right) = 0$, but e^{π_A} or $e^{\frac{\int v\,dp}{RT}} = f_A$ by definition of fugacity where f_A is the fugacity of pure component A at the given temperature and total pressure.

The validity of this rule has been the subject of a number of investigations and, as one would expect, it is far from exact. It would lead us too far afield to enter into any discussion of this point.

K_{p_0} may now be calculated directly from K_p by means of the relation

$$K_{p_0} = K_p \frac{\left(\frac{e^{\pi_C}}{p}\right)^c}{\left(\frac{e^{\pi_A}}{p}\right)^a \left(\frac{e^{\pi_B}}{p}\right)^b} \tag{9}$$

In the absence of an equation of state for mixtures of carbon monoxide, hydrogen, and methanol, the writers have attempted to treat their data by means of Equation 9. Accurate equations of state are available for carbon monoxide and hydrogen, but not for methanol. Van der Waals' equation has been used for all three gases, the constants a and b being evaluated from the best published values of critical pressure and temperature.

Note—It should be noted that $\int v\,dp$ cannot be directly obtained from van der Waals' equation. It is necessary to change to v as the independent variable. This is liable to lead one into error because the lower-limit of the integral has already been substituted. It can easily be shown that if dp is changed to dv and the integral then evaluated, as an indefinite integral, the expression e^{π} should be multiplied by RT. In other words, for this case $f = RTe^{\pi}$.

A few calculations on hydrogen using the Beattie-Bridgman equation of state gave results but slightly different from those using the much simpler equation. Since methanol is the most important component and, since Equation 9 is only a rough approximation anyway, it did not appear worth while to use any more complex equations of state for hydrogen and carbon monoxide.

Values of K_{p_0} calculated in this way are given in the last column of Table II. From this table it will be seen that the effect of pressure on the equilibrium constant at the pressure of these experiments is very considerable. In Figures 4 and 5 the data are shown in the form of graphs of $\log_{10} K_p$ and $\log_{10} K_{p_0}$, respectively, as a function of $1000/T$. The best straight line has been put through the points, omitting from consideration points from runs earlier than No. 15, excepting No. 8. It will be noted that all these earlier runs were made with a zinc-chromium catalyst, and they are believed to be less reliable than the later runs, owing to the greater amount of side reactions. Considered by themselves, without reference to the later experiments with a zinc-copper catalyst, these points are fairly consistent. Thus, 9A and 10 were at considerably higher space velocities and it is probable that equilibrium was not attained. The two synthesis runs, $9B_1$ and $9B_2$, check well and give somewhat lower values of K_p than the decomposition run 12, as would be expected. Furthermore, the average of these three runs agrees fairly well with the result obtained by Lacy, Dunning, and Storch at 300° C. It appeared to the present writers, however, that side reactions would tend to give too low K_p values and that therefore the higher values obtained with the zinc-copper catalyst were closer to the truth. Logically, run 8 should also be omitted, but since it falls nicely into line with the later runs using a zinc-copper catalyst, it has been retained. The equations of the two straight lines, determined by the method of averages, are:

$$\log_{10} K_p = \frac{7974}{T} - 17.045$$

$$\log_{10} K_{p_0} = \frac{7358}{T} - 16.312$$

From the K_{p_0} values standard ΔF's have also been calculated and from them the integration constant, I, of the standard free-energy equation using the same thermal data used by Smith and Branting (*19*). The results are given in Table IV.

Table IV—Calculation of Integration Constant of Free-Energy Equation

Run	ΔF^0	I
8	11400	-52.4
15	5620	-54.7
16	6100	-54.0
17	7070	-53.8
18	7310	-53.2
19	9840	-52.6
20	9750	-52.8
22	6100	-54.0
23	8590	-54.1
	Av.	-53.50

Using the average value of I, we get for the final K_{p_0} equation,

$$\log_{10} K_{p_0} = \frac{4570}{T} - 9.010 \log_{10} T + 0.00312\, T + 11.70$$

In Table V are compared values of K_{p_0} calculated from this equation with those obtained by other investigators. The data of Lacy, Dunning, and Storch were extrapolated beyond 300° C. by using the K_{p_0} values calculated from their best K_p values at 250° and 300° C. to give an average I, just as in the treatment of the data of the present writers. The data of Newitt, Byrne, and Strong (*17*) were extrapolated by calculating K_p from their equation at 10-degree intervals from 280° to 320° C. (about their experimental range), converting these to K_{p_0} assuming an average pressure of 80 atmospheres and then getting an I value for each K_{p_0} just as previously done for the writers' own data.

Table V—Calculated Values of K_{p_0} Obtained from K_p Given by Various Investigators

Investigator	Pressure Atm.	$K_{p_0} \times 10^3$ at 250° C.	$K_{p_0} \times 10^4$ at 300° C.	$K_{p_0} \times 10^5$ at 350° C.	$K_{p_0} \times 10^6$ at 400° C.
Authors	170	3.7	4.6	6.3	13.8
(*13*)	50	1.3	1.35	2.0	3.8
(*19*)	1.0	5.9	6.4	7.9	20
(*17*)	70–100	1.15	1.2	1.8	3.5
(*14*)	204				9.4
(*1*)	150				12.1
(*3*)	180				11.2

It will be noted that the present writers' results are intermediate between those of Smith and Branting obtained at 1 atmosphere and those of the two pairs of investigators who worked at higher pressures, being, however, much closer to the former. The writers' value for 400° C. is in pretty good agreement with those of the three investigators who have reported experimental data for this temperature only.

The writers believe that the results of Newitt, Byrne, and Strong and of Lacy, Dunning, and Storch are too low in spite of their excellent agreement. In the first place, the present writers have repeatedly obtained yields of methanol at temperatures from 350° to 400° C. and at fairly high space velocities (from 5000 to 30,000), which yields are greater than those corresponding to the equilibrium obtained by these investigators. In the second place, they did not take any account of side reactions, but assumed that the exit gas had the same composition as the inlet gas. In the experiments of the present writers this was far from true, as a glance at Table III will show. With a catalyst containing chromium the writers' results show that considerable amounts of dimethyl ether are formed at low space velocities. This is in agreement with the results obtained by Brown and Galloway (*4*). Newitt, Byrne, and Strong used a zinc chromate catalyst, but do not mention ether formation, nor did they report any systematic analyses of their off-gases. Lacy, Dunning, and Storch did not analyze their off-gases and so were obliged to assume them to have the same composition as the inlet gas. The present writers' experience indicates that this might easily give a K_p which is much too low. Although no evidences of any ether formation were observed with their zinc-copper catalyst, yet there were appreciable amounts of carbon dioxide and methane formed. Because of the very great shrinkage in gas volume due to the high conversion to methanol obtained at temperatures of 300° C. and lower, even a small amount of side reactions will greatly affect the percentage of hydrogen and carbon monoxide at equilibrium and, therefore, the equilibrium constant. Thus, if for run 17 one calculates the equilibrium constant on the assumption that the off-gases are hydrogen and carbon monoxide in the

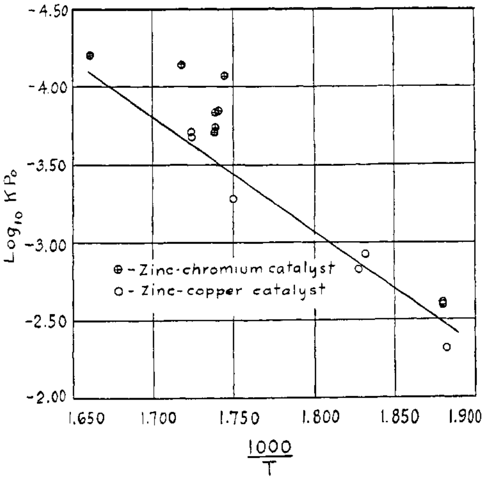

Figure 5—$\log_{10} K_{p_0}$ Versus $1000/T$

stoichiometric ratio, the result obtained is only one-half the value based on the actual gas analysis. It should also be noted that the purity of the condensate produced is not a safe criterion of the absence of side reactions, as is shown by the data in Table III.

If dimethyl ether was formed in the experiments of Smith and Branting—and one would certainly expect it to be since they used a chromate catalyst and since the dehydration of methanol occurs without volume change—their results would probably be high, because the tests of the present writers show that dimethyl ether would be determined as methanol by the analytical method of Smith and Branting. Allowing for this fact would bring their results into quite close agreement with those of the present writers.

It is difficult to estimate the effect of side reactions on the establishment of equilibrium. It is obvious, however, that a true equilibrium cannot be established with respect to the methanol reaction when side reactions are proceeding simultaneously at a considerable distance from equilibrium. The question as to how closely one comes to the methanol equilibrium in spite of side reactions involves the relative rates of the various reactions concerned and cannot be readily answered. The ideal solution to the problem is to find a highly specific catalyst. Some improvement could doubtless be made with the present catalysts by choosing the proper conditions to minimize the relative amount of side reactions. Decrease in temperature or increase in space velocity seems to favor the main reaction relative to the side reactions, but both are, of course, less favorable to the attainment of equilibrium.

Although the writers' equilibrium constants may still be somewhat low owing to the influence of side reactions, they believe that further and more accurate experimental work will not alter them greatly. The results further strengthen the belief that the experimentally determined equilibrium constants are of the right order of magnitude and that those calculated by means of the third law and the best available heat data are incorrect.

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Condensation Reactions of Acetaldehyde over Certain Oxide Catalysts at Pressures from 1 to 500 Atmospheres of Hydrogen[1]

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Apparatus is described for carrying out reactions of organic liquids under pressure in the vapor state in an atmosphere of hydrogen. The experimental work is reported in two parts—one dealing with the effect of pressure, temperature, rate of flow, composition of catalyst, water content, etc., on the ratio and rate of formation of hydrogen and ethylene; and the other with the effect of these variables on the character of the liquid products.

The liquid products are in all cases complicated mixtures which were partially fractionated and then reduced over nickel catalysts. A list of compounds and yields are given ranging from ethyl alcohol and acetaldehyde through esters of acetic, butyric, and caproic acids and alcohols higher than octyl. Equations suggesting probable mechanisms are given for these products.

When ethanol is passed over dehydrogenating catalysts such as zinc oxide at temperatures of 300° to 400° C. it is dehydrogenated to acetaldehyde. If this reaction takes place under a sufficient pressure of hydrogen practically no acetaldehyde but substances of higher molecular weight are to be found in the reaction products. The results obtained in a beginning of an experimental study of these reactions are the basis for the present paper.

Apparatus

The essential parts of the apparatus used in carrying out the reactions under pressure were a pump, a vaporizer, a catalyst chamber, a condenser, a receiver, a hydraulic gage, and the necessary valves, tubing, and connections. The pump had two cylinders, each having an internal volume of 150 ml., one of which at any given time was delivering and the other receiving liquid. The liquid could be delivered at rates from 60 to 600 ml. per hour against pressures up to 1000 atmospheres. The vaporizer was a chrome-vanadium steel bomb similar in construction to the catalyst chamber but having an internal volume of only 50 ml. It was filled with $^1/_4$-inch (6.4-mm.) steel balls. The catalyst chamber was essentially the same as that supplied by the American Instrument Company as their standard catalyst chamber for ammonia synthesis on a laboratory scale but modified in that external heating was used and the catalyst holder had a capacity for about 75 ml. of catalyst. The condenser was a 3-foot (91.4-cm.) length of $^1/_4 \times ^1/_{16}$ inch (6.4 × 1.6 mm.) steel tubing in a jacket through which water was circulated. The receiver was similar in design to the catalyst chamber except that it had an internal volume of 200 ml. and was of somewhat lighter construction. It was provided with an outlet at both top and bottom so that either gas or liquid could be withdrawn from the system. The catalyst was in the form of pellets and was prepared by the ignition of zinc

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