

Summary and Conclusion

The pyrosulfate fusion as a means for the quantitative determination of tantalum and columbium has been studied with results and conclusions as follows.

1. When fused at a low temperature (about 650°) iron and titanium are completely separated from the tantalum by digestion near the boiling temperature with 3 *N* hydrochloric acid. The tantalic and columbic acids are left in the insoluble portion.

2. When the fusion mixture is held at 835 to 850° for ten to fifteen minutes, the columbium only is dissolved by fuming with concentrated sulfuric acid. The solution may be diluted without precipitation if the cold acid mixture is slowly poured into water kept cold with ice or running water.

3. A method of procedure for the determination of tantalum and columbium is given.

4. The possibility of more economic extraction and separation of tantalum and columbium is indicated in the method used for the removal of iron and titanium and in the fact that the sulfuric acid solution may be diluted without precipitation of columbium.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE EQUILIBRIUM BETWEEN METHANOL, CARBON MONOXIDE AND HYDROGEN. PRELIMINARY PAPER¹

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Introduction

Although our work on the equilibrium between methanol, carbon monoxide and hydrogen is still in progress, it has been decided to present the results so far obtained. The results heretofore available are very conflicting and no direct experimental measurements of equilibrium appear to have been made. The many inquiries which have been received concerning the data indicate the general interest and practical importance attached to the thermodynamic properties of methanol.

Published values of the free energy of methanol have been obtained in several ways. Kelley⁴ has calculated his value from the specific heat of

¹ Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Presented before the Division of Gas and Fuel Chemistry at the 75th meeting of the American Chemical Society, St. Louis, Missouri, April 17, 1928.

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⁴ Kelley, *Ind. Eng. Chem.*, 18, 78 (1926).

liquid methanol down to liquid-air temperatures, extrapolating to 0°K. and using the Third Law of Thermodynamics. Christiansen⁵ has used a Nernst approximation formula, and also his preliminary measurements of equilibria in the two sections $\text{HCOOCH}_3 + 2\text{H}_2 = 2\text{CH}_3\text{OH}$ and $\text{CH}_3\text{OH} + \text{CO} = \text{HCOOCH}_3$. The calculation of Smith⁶ involved substantially the same data that were used by Kelley, except for the substitution of a better value for the high temperature specific heat of methanol vapor. The data of Kelley were at that time considered more reliable than those of Christiansen, partly because of the latter's own statements regarding the preliminary nature of his equilibrium measurements. While the calculations of Kelley and of Smith were in substantial agreement, they were widely different from Christiansen's results. Although not much confidence can usually be placed in the results from the Nernst approximation formula, the formula as presented by Christiansen gave results in fair agreement with his equilibrium measurements.

The equilibrium constant $(\text{CH}_3\text{OH})/(\text{CO})(\text{H}_2)^2$, where concentrations are expressed in terms of the partial pressures in atmospheres, is 10.6 at 200° according to Smith's calculation from Kelley's data. Christiansen's equilibrium data⁷ give 0.055 at this temperature. The Nernst approximation formula, as proposed by Christiansen, gives 0.042. Recently Morgan, Taylor and Hedley⁸ have discussed the results of the Nernst formula which Audibert and Raineau⁹ state to be in substantial agreement with the results they obtained in practical operation at high pressures. They note that the discrepancy between the results obtained from this formula and from the equation derived by Kelley increases with increasing temperature. At 600°K. the formula gives a constant about one-hundredth of that calculated from Kelley's results.

Apparently, apart from the preliminary equilibrium measurements of Christiansen, the only direct experimental estimates of the methanol equilibrium have been obtained from results of actual operation of the methanol process at high pressures—operations which were of course neither designed for nor well adapted to furnishing accurate equilibrium data. In addition to the inherent difficulties in precise measurement at high pressures, the theoretical accuracy obtainable on measurements of this equilibrium at high pressure is unsatisfactory; for example, a relatively small error in determination of the conversion of carbon monoxide to methanol would, at very high pressures, introduce a disproportionately large error into the value of the equilibrium constant so derived. Of

⁵ Christiansen, *J. Chem. Soc.*, **123**, 413 (1926).

⁶ Smith, *Ind. Eng. Chem.*, **19**, 801 (1927).

⁷ Christiansen in his paper evidently expresses concentrations in moles per liter and uses the reciprocal of the constant used here.

⁸ Morgan, Taylor and Hedley, *J. Soc. Chem. Ind.*, **47**, 117T (1928).

⁹ Audibert and Raineau, *Ann. Office Combustibles Liquides*, **1927**, Part 4.

course, standard free energy data cannot be obtained from equilibrium measurements at high pressures without a much more complete knowledge of the equations of state of the separate gases, both in the pure state and in the mixtures, than is at present available. Also, when a considerable amount of reaction is taking place on the catalyst, the temperature control is likely to be poor. In view of the importance of this reaction, the conflicting nature of the existing equilibrium data makes a direct determination of the standard free energy of methanol highly desirable.

Experimental Procedure

At 300° and a total pressure of 1 atmosphere, Kelley's data would give the limiting (equilibrium) decomposition of methanol to CO and 2H₂ as about 96.4%. With an active catalyst, therefore, it should be possible under these conditions to determine the limiting decomposition of methanol vapor and, under the same conditions, to determine readily the maximum yield of methanol from mixtures of carbon monoxide and hydrogen.

Our method was first to pass pure methanol vapor over an active catalyst at a rate slow enough to give substantially equilibrium conditions. This set a maximum value on the constant of the reaction. Second, a mixture of carbon monoxide and hydrogen was passed over the catalysts at a rate slow enough to give the maximum yield of methanol. The latter experiment set a minimum limit on the value of the constant.

The methanol used was made from the commercial "absolute" product which we freed from aldehydes, ketones and water according to the method described by Danner and Hildebrand¹⁰ for ethyl alcohol. One catalyst used was zinc oxide made from pure, freshly precipitated carbonate. Another catalyst was made by adding chromic acid to purified zinc oxide, in the atomic proportions 4Zn:1Cr.¹¹ About 600 cc. of 8-mesh per inch catalyst was used in each experiment. The CO-H₂ mixture was made by adding electrolytic hydrogen from a cylinder to water gas generated by a small generator available at this Laboratory. The gas mixture was pumped from a 7-cu.m. gas holder through a liquid-air cooled trap to remove sulfur compounds and all heavy gases, over heated copper to remove oxygen and into a high-pressure cylinder.

In our early decomposition experiments, when we were guided by the data of Kelley, methanol vapor at 1 atm. pressure was passed over the catalyst. It was soon found, however, that the final concentration of methanol resulting after passage over the catalyst, even at very slow rates, not only was much smaller than was expected, but was always much larger than the maximum yield of methanol from the CO-H₂ mixture. It was decided that this was due either to some adsorption effect on the catalyst or to the fact that the mechanism of the reaction changes to a higher order at very low pressures of methanol. The reaction should obviously be started at somewhere near equal distance from equilibrium in the decom-

¹⁰ Danner and Hildebrand, *THIS JOURNAL*, **44**, 2824 (1922).

¹¹ See Smith and Hawk, *J. Phys. Chem.*, **32**, 415 (1928), for method of catalyst preparation.

position and in the synthesis experiments. We therefore introduced methanol vapor into the CO-H₂ mixture by passing the latter through a saturator containing purified methanol at the temperature of a liquid ammonia bath (-38°). The vapor pressure of methanol at this temperature was still over 40 times the equilibrium pressure, so that the experiments were thus started definitely on the methanol side of equilibrium.

Fig. 1 shows the apparatus used. The gas from the cylinder, previously purified, passes into the apparatus at *a*. The flow of gas is adjusted by the head in a tube of water, *b*. The gas then passes through heated platinized asbestos in *c* to remove oxygen, then through a liquid-air trap, *d*, to remove all heavy gases, through the methanol saturator, *e*, surrounded by a bath of liquid ammonia, through the first catalyst tube, *f*,

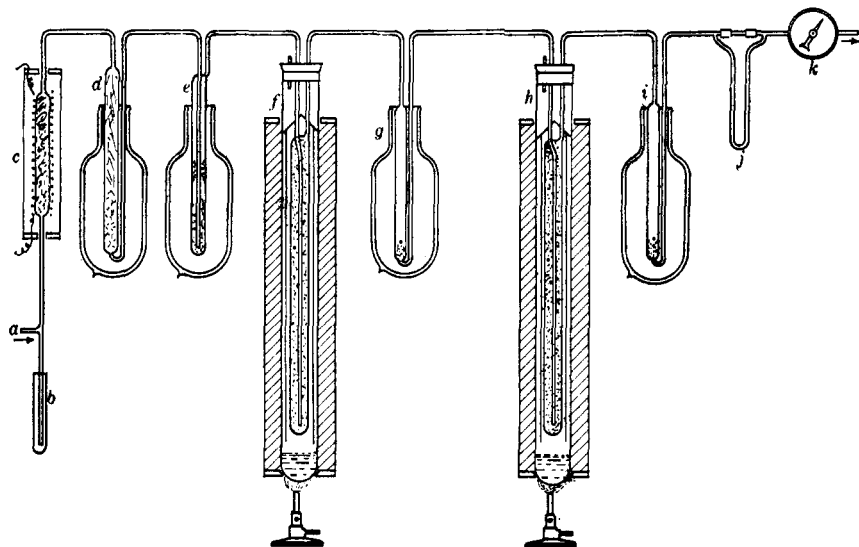


Fig. 1.—Apparatus for measuring equilibrium in the methanol reaction.

f, and through a liquid-air trap, *g*, to condense the remaining methanol. The gas then passes through a second catalyst tube, *h*, and the yield of methanol is caught in a second liquid-air trap, *i*. The gas emerging from the apparatus is passed through a flow meter, *j*, and a carefully calibrated meter,¹² *k*, in order to determine its volume. Samples of the gas after passage over each catalyst were collected and carefully analyzed to determine the partial pressures of carbon monoxide and of hydrogen with which the methanol came to equilibrium.

The catalyst was maintained at a constant temperature by surrounding it with the vapor of boiling benzophenone. The catalyst tubes were shielded with thin sheet-iron tubes and umbrellas, as recommended by the Bureau of Standards.¹³ The benzophenone was purified by distillation before use and the boiling temperature was checked with a carefully calibrated resistance thermometer.

¹² In regard to calibration and use of wet-test meters, see Bureau of Standards Circular No. 309 (1926), and Technologic Paper No. 36 (1926).

¹³ Bureau of Standards Scientific Paper, No. 339 (1919).

At the beginning of an experiment, in order to bring the catalyst to equilibrium with the gas mixture used, the apparatus was always completely purged with the gas to be used, before the yields of methanol were collected.

The methanol yields were determined colorimetrically, according to a method which suggested itself to us from the work of Wright.¹⁴ The method depends upon oxidation of the methanol to formaldehyde with permanganate. The excess of permanganate is destroyed by oxalic acid, and the color is developed upon the addition of a modified Schiff's reagent, prepared as described by Wright, which forms a blue compound with the formaldehyde. It was determined that no detectable amounts of formaldehyde were formed directly by the catalyst, and that other alcohols and dimethyl ether¹⁵ do not interfere with the test in this case. Since no other known by-products of the methanol reaction which could have been present in the solution used for the methanol determination would have interfered, the method may be regarded as an absolute determination of the methanol. Careful checks were made upon several series of known solutions and it was shown that by the colorimetric method the concentration of methanol in aqueous solutions as dilute as 1 part in 10,000 could be determined with an accuracy of 1% or better. In each determination a series of standard solutions was made up and treated in exactly the same way as the unknown solution. A calibration curve of intensity of transmitted light against the concentration of solution was plotted for interpolation purposes and the unknown solutions were always compared with a standard solution whose concentration was very close to that of the unknown solution. Since the colors were compared in a colorimeter by transmitted light, the curve of concentration against intensity was approximately logarithmic, as given by Beer's Law. Although it took a short time for the color to develop (and the color, of course, faded upon long standing), a comparison of the color in a standard solution with that in the unknown solution after each had stood for forty-five to sixty minutes gave the same result as did a comparison made an hour or more later.

The condensers containing the yields of methanol, after removal from the apparatus, were maintained at about 1° above the temperature of carbon dioxide snow until the small amount of carbon dioxide which is formed in the reaction and subsequently condensed, had evaporated from the condenser. At this temperature the vapor pressure of methanol is so low that no appreciable quantity of it could be lost. Also, there was always water present from the reaction in amount comparable to that of

¹⁴ Wright, *Ind. Eng. Chem.*, **19**, 750 (1927).

¹⁵ McKee and Burke [*Ind. Eng. Chem.*, **15**, 788 (1923)] were able to determine the equilibrium between methanol and dimethyl ether using an Al_2O_3 catalyst at 350°; and Smith and Hawk [*J. Phys. Chem.*, **32**, 415 (1928)] showed that dimethyl ether is probably formed from methanol vapor at 1 atm. on chromium oxide catalysts. However, it is known that zinc oxide probably would give no appreciable quantities of ether at 300° [Adkins and Perkins, *J. Phys. Chem.*, **32**, 221 (1928)]. Probably zinc oxide-chromium oxide catalysts which contain excess of zinc oxide would be relatively inactive also. If, as would be supposed in the absence of complete experimental information, the formation of the ether from methanol is a higher order reaction than is the formation of CO and H_2 from methanol, the rate of formation of ether from methanol at very low pressures would be negligible compared to the rate of formation of CO and H_2 . Furthermore, dimethyl ether if it had been present would doubtless have disappeared during the removal of CO_2 from our condensed product as described below. At any rate, we showed by actual tests that dimethyl ether does not enter into the reaction we used to determine methanol. (Since this test for methanol is so sensitive, it is of course necessary to assure that the dimethyl ether used in the test does not contain traces of methanol.)

the methanol. Exactly 5 cc. of water was introduced into the condenser, which was then sealed, allowed to come to room temperature and shaken to dissolve the methanol into a uniform solution. The methanol in aliquot portions of these solutions was then determined, as described above.

Experiments showed that, with the type of liquid-air cooled receiver used, no methanol escaped even at much higher rates of gas flow than we had ever used in equilibrium measurements.

Since it soon became evident that the equilibrium decomposition of methanol at 304.4° was relatively far more than the expected 96.4%, it was necessary when working at atmospheric pressure to deal with rather small quantities of methanol. In spite of this, however, it was thought better to work at atmospheric pressure for the reasons mentioned and since the small quantities of methanol could nevertheless be determined accurately.

Experimental Results

The experimental results are presented in Tables I and II. In a single experiment a total gas volume of from 17 to 30 liters was passed over the

TABLE I
RESULTS OF EQUILIBRIUM MEASUREMENTS

Expt. no.	Synth. or decompn.	Av. barom. atm.	Temp. of catalyst, °C.	Rate of gas flow, cc./min.	CH ₃ OH, g./cu. m. of gas at STP	CH ₃ OH/(CO)(H ₂) ²	<i>I</i>
1	s	0.967	303.9	9.0	0.0456	3.73×10^{-4}	-53.62
2	s	.963	303.8	4.0	.0505	4.19×10^{-4}	-53.85
3	s	.974	304.3	1.8	.0562	4.27×10^{-4}	-53.92
4	s	.966	303.9	1.6	.0520	4.27×10^{-4}	-53.89
4a	d	.966	303.9	1.6	.0767	6.30×10^{-4}	-54.66
5	s	.968	304.0	1.7	.0681	5.56×10^{-4}	-54.42
5a	d	.968	304.0	1.7	.0695	5.67×10^{-4}	-54.46
6	s	.963	303.8	1.7	.0672	5.57×10^{-4}	-54.41
6a	d	.963	303.8	1.7	.0672	5.57×10^{-4}	-54.41

TABLE II
AVERAGE ANALYSIS OF GAS

Constituent	H ₂	CO	CO ₂	CH ₄	N ₂
Volume, %	56.7	29.4	0.6	1.9	11.4

catalyst. The methanol yields in Table I have been corrected, on the basis of the gas composition as given in Table II, for the volume of carbon dioxide caught in the liquid-air condensers. These yields are thus those which would be obtained from 1 cubic meter of a gas having the composition given in Table II. The analyses of the gas from different experiments were, within the limits of the error in gas analysis, not significantly different. We have thus preferred to use an average gas composition throughout. An uncertainty in the values of the equilibrium constants results from the gas analysis. The best results obtainable with this gas, using any standard method of gas analysis, may be uncertain to about 1% of the amount of carbon monoxide and about 0.5% of the amount of hydrogen. In the product (CO)(H₂)², and thus in the equilib-

rium constant, there may be introduced in this way an error of about 2%. Further, since the ordinary wet-test meter was used to measure the total gas volumes, an error of 2% or so may also be introduced on account of change in the vapor pressure of the water and change in level of the water in the meter with variations in the room temperature during the course of an experiment—about one week. The calibration of the meter was made at the rates of gas flow used in the equilibrium measurements and in a room where the temperature was usually nearly constant. Of course, there is also an error involved in assuming that all three gases obey the perfect gas law from room temperature to 300°. However, this error is doubtless inconsiderable. In further work it is planned to eliminate these uncertainties by constructing a special gas-analysis apparatus and using a better means of measuring the gas volumes.

It was found that evacuation of the catalysts, between experiments, considerably improved their activity, probably on account of the removal of the small amounts of carbon dioxide and water adsorbed during the reaction. The promoted catalyst did not seem to be as much affected by adsorbed carbon dioxide and water as did the pure zinc oxide catalyst. It is thought that since the catalyst used in experiment 5a was pure zinc oxide that had not recently been evacuated, the constant from this experiment is somewhat high. The last two pairs of experiments (Nos. 5 and 5a, 6 and 6a) were performed most carefully and obviously came closest to equilibrium. As the best value of K we take that from Expts. Nos. 6 and 6a—namely, 5.57×10^{-4} at 303.8°.

Although the rates of gas flow were very low, and perhaps in many cases unnecessarily so, the linear rate of gas flow through the small diameter tubing connecting the various units in the apparatus was great enough to avoid possible complications due to self-diffusion of the gases.

The values, in the last column of Table I, of the integration constant, I , of the free energy equation were obtained through use of the best available heat data as given by Smith.¹⁶ The equation expressing the free energy change in the reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ is, then, $\Delta F = -20,857 + 41.17T \log T - 0.01423T^2 - 54.42T$. The heat data would seem to be reliable, although they have been questioned.⁸ This equation gives the standard free-energy change for this reaction as 16,070 cal. at 700° K., which may be compared with the value 8930 cal. used by Lewis and Frolich¹⁷ in their paper giving the practical yields obtained in the methanol process. Our data give $K = 6.51 \times 10^{-4}$ at 300°; the equation given by Audibert and Raineau gives $K = 11.3 \times 10^{-4}$; Christiansen's data give 4.27×10^{-4} ; and Kelley's data give 8.2×10^{-2} . If Audibert and Raineau's equation was derived from their work at high pressures and the

¹⁶ Smith, *Ind. Eng. Chem.*, **19**, 801 (1927).

¹⁷ Lewis and Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928).

equilibrium constants calculated without the use of fugacities, their constants would come out too high. Christiansen's data are fairly close to ours. However, the difference between our data and the values calculated from Kelley's data is unaccountably large. Various possible explanations for this discrepancy have been considered, but so far no satisfactory explanation can be given. In further work we hope to obtain the equilibrium constant more accurately and at several temperatures and thus throw some light on the question.

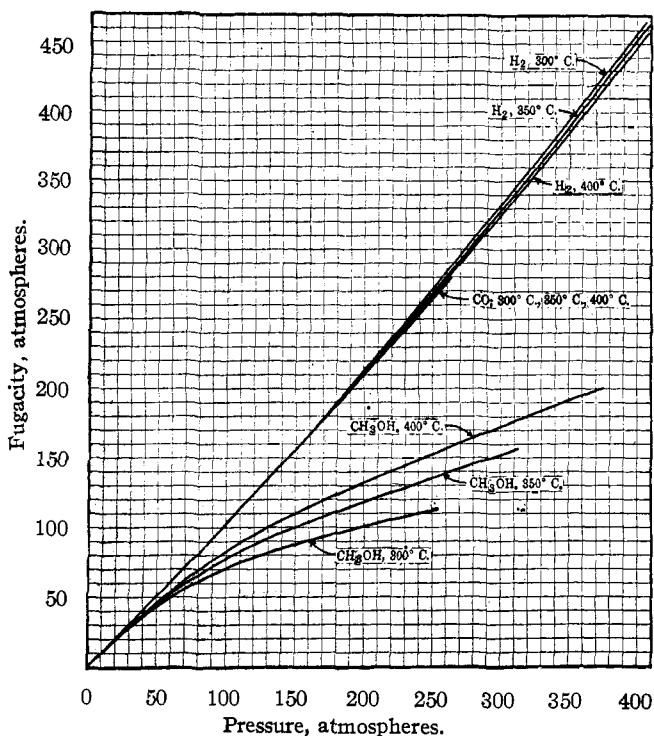


Fig. 2.—Fugacities of H₂, CO and CH₃OH.

It may be of interest to compare briefly our theoretical yields with the yields of methanol which have been obtained in the practical operation of the methanol process. In order to do this it is necessary first to estimate the fugacities of the three gases involved. The results of these calculations are presented in Fig. 2. The data for carbon monoxide were calculated from van der Waals' equation, with $a = 1.487 \times 10^6$ and $b = 39.87$, derived from compressibility data of Amagat¹⁸ which are given up to 400 atm. at 20°. The data for hydrogen were derived, using the rule

¹⁸ Amagat, *Ann. chim. phys.*, [6] 29, 68 (1893).

of Lewis and Randall,¹⁹ from compressibility data of Bartlett, which are given at intervals up to 1000 atm. at 300 and 400°. ²⁰ The data for methanol were calculated from van der Waals' equation, with $a = 9.534 \times 10^6$ and $b = 76.06$, derived from compressibility data of Ramsay and Young²¹ which are given up to 78 atm. at 240°. Although the fugacity data are admittedly rough, their use will give better results at high pressures than would the use of the pressures. The fugacities of hydrogen and of carbon monoxide are in general somewhat higher than the pressures

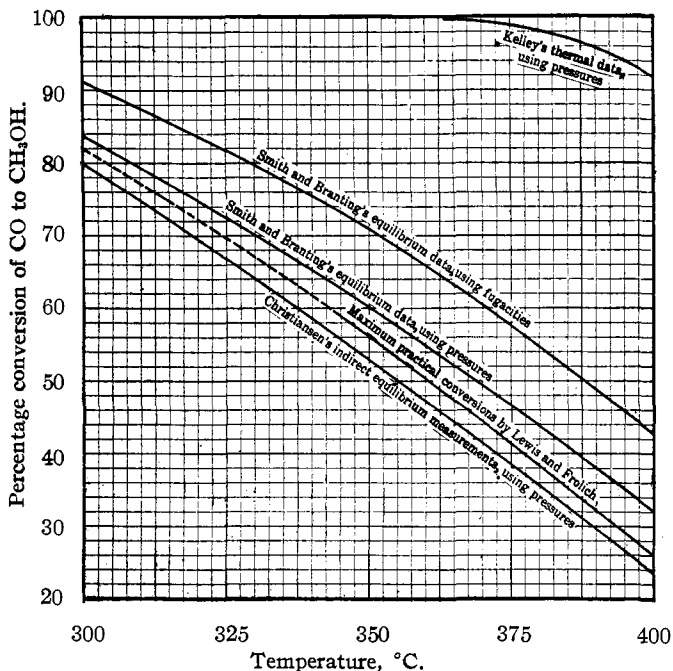


Fig. 3.—Comparison of conversions of CO to CH₃OH as calculated from thermodynamic data and as obtained practically, at several temperatures and at a total pressure of 204 atm. with a gas containing 26% of CO and 70% of H₂.

whereas the fugacities of the methanol are considerably lower than the pressures, as would be expected. This, in each case, results in larger practical yields of methanol than would be predicted from the pressures.

In Fig. 3 are presented comparisons of practical conversions of carbon monoxide to methanol, with the maximum possible conversions predicted

¹⁹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1928, p. 197.

²⁰ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 5.

²¹ *Ibid.*, p. 436.

from various thermodynamic data.²² The practical yields are taken from Lewis and Frolich. It is seen from the figure that the practical conversions are definitely lower than those predicted from our data, irrespective of any reasonable assumptions as to the fugacities of the gases under these conditions. Lewis and Frolich state that their data at 300° are uncertain. Although it is not possible to draw from these comparisons any definite conclusions regarding the reliability of the thermodynamic data, the comparisons between the predictions from our data and the yields obtained at high pressures are as one would expect. A further comparison may be made between our $K = 2.07 \times 10^{-5}$ and the estimation of $K = 1.1 \times 10^{-5}$ at 400° made by Brown and Galloway²³ from their work on the production of methanol at 180 atm. pressure. It is to be noted in connection with the yields obtained by Lewis and Frolich that, if the gas composition of 26% of carbon monoxide and 70% of hydrogen refers to the original gas, the concentrations of reactants during reaction, especially at the higher temperatures, would be somewhat less because of side reactions. If this were taken into account, the practical yields would be somewhat closer to the theoretical. If the results of the high-pressure work can be relied upon, it would seem that the heat data we have used in the equation giving the temperature function of the free energy are not seriously in error, since the theoretical and experimental curves parallel each other between 300 and 400°.

The value of K we obtained at 304° would seem to have a maximum uncertainty of about 10%; the probable error is not more than about 5%.

Of course, before thermodynamic data can be accurately applied to high pressure work, it would be necessary to know the equations of state for the three gases involved, in mixtures of different compositions. However, the thermodynamic data here presented, together with estimated fugacities, will probably give results which, at present, are sufficient for all practical purposes. A more immediate interest in obtaining accurate thermodynamic data on this reaction at several temperatures would be to show wherein the error lies in the calculations from Kelley's data.

Summary

1. The equilibrium between methanol, carbon monoxide and hydrogen has been experimentally determined at 304° and a total pressure of 1 atmosphere, by a direct method.

2. The equilibrium constant, $K = \text{CH}_3\text{OH}/(\text{CO})(\text{H}_2)^2$, is 5.57×10^{-4} at 303.8°, with a probable error of $\pm 5\%$. Calculations from Kelley's

²² The practical conversions used are to be regarded as the maxima obtained in the particular tests referred to. There is no evidence from the curves of conversion against space-velocity, that these conversions are the maximum possible.

²³ Brown and Galloway, *Ind. Eng. Chem.*, **20**, 960 (1928).

low temperature specific heat measurements, extrapolated from room temperature with aid of the best available heat data, give a constant more than 100 times this value. Christiansen's indirect equilibrium measurements give a constant about 34% smaller than our value.

3. The equation for the standard free-energy change in the methanol reaction, derived from our equilibrium measurements and the best available heat data, is $\Delta F = -20,857 + 41.17T \log T - 0.01423T^2 - 54.42T$.

4. The yields of methanol at high pressures, as obtained practically and as predicted by our thermodynamic data, compare favorably.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. VIII. THE DETERMINATION OF CHROMIUM IN THE PRESENCE OF MANGANESE, IRON AND VANADIUM

BY H. H. WILLARD AND PHILENA YOUNG

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Introduction

The present volumetric methods for chromium depend upon its oxidation to the hexavalent form by an excess of some suitable reagent and its subsequent reduction, after removal of the excess oxidizing agent, by standard ferrous sulfate added either (1) directly to an end-point which may be determined either electrometrically, with diphenylamine or diphenylbenzidine¹ as internal indicator, or with ferricyanide as external indicator, or (2) in excess, the excess being determined by back titration with standard dichromate or permanganate. In the absence of oxidizing agents such as ferric iron, excess iodide may be used as the reducing agent, the iodine liberated being titrated with thiosulfate. A method using arsenite² and another with excess arsenite, followed by back titration with bromate have been described.³ If persulfate in the presence of silver ions⁴ is employed to oxidize the chromium, the excess is destroyed by boiling, and moderate amounts of manganese, converted into permanganate, are reduced to manganous salt by the addition of chloride ions and further boiling. If permanganate is the oxidizing agent, a filtration is always required. In certain cases oxidation is effected by per-

¹ The authors have described the use of diphenylbenzidine as an indicator in the titration of chromic plus vanadic acids with ferrous sulfate, Willard and Young, *Ind. Eng. Chem.*, **20**, 769 (1928). The results using this indicator are the same when chromic acid alone is titrated with ferrous sulfate.

² Zintl and Zaimis, *Z. angew. Chem.*, **40**, 1286 (1927); **41**, 543 (1928).

³ Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1910).

⁴ Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 719 (1916).