

duced. On the other hand, from paraffinic crudes so-called aromatic products may be formed—as, for example, a highly antiknock gasoline from a very paraffinic gas oil. Even from the same gas oil paraffinic burning oil and antiknock gasoline may be made. Consequently, from any given supply of crude the products of the quality desired may be produced by refineries employing hydrogenation.

Table VI—Production of Antiknock Gasolines by Hydrogenation

	MIDCONTINENT LIGHT GAS OIL	WEST TEXAS CYCLE GAS OIL
FEED STOCK:		
° A. P. I.	37.4	30.3
I.B.P., ° F.	474	400
Per cent at 460° F.	2.5	56.0
Per cent at 550° F.	89.0	..
Per cent at 650° F.	..	..
F.B.P., ° F.	618	612
Sulfur	0.153	0.192
Aniline point	161	102
HYDROGENATED PRODUCT:		
Yield, per cent by volume	89.9	94.5
° A. P. I.	55.4	39.8
I.B.P., ° F.	95	110
Per cent at 212° F.	35.0	13.5
Per cent at 284° F.	54.0	25.0
Per cent at 356° F.	72.5	..
Per cent at 374° F.	79.0	50.5
Per cent at 400° F.	87.0	70.5
F.B.P., ° F.	428	436
Knock rating as per cent iso-octane	72.6	82.2
in <i>n</i> -heptane	17.7	9.0
Dissolved gum, per cent	0.013	0.005
Sulfur, per cent	0.013	0.005

(6) The flexibility of the process is very marked as to character of the charging stock and quality of product produced. Examples have been given showing how the same plant may be used (a) for producing gasoline and gas oil, (b) very paraffinic high A. P. I. gravity burning oils from mixed-base gas oils, (c) color- and gum-stabilizing and desulfurizing highly cracked naphthas, (d) production of paraffinic lubricants from mixed base stocks, and (e) production of antiknock, high-compression gasoline from paraffinic gas oils. Further, from the above examples it may be seen that from practically any grade of crude oil products of any desired quality may be produced.

(7) The hydrogenation process uses compressed hydrogen, a rather costly material. Offsetting this are the following factors: (a) the ability to balance crude run to white product demand, (b) the premium quality of products produced, (c) the low value charging stocks that may be used, and (d) the extreme utility of the process, due to its flexibility, especially where types of crudes to be refined and markets to be supplied vary from time to time.

Table VII—Influence of Character of Feed Stock on Knocking Tendency of Hydrogenated Gasolines

Gasoline yield, per cent	89.9	91.4	88.0	89.0
Aniline point of charge stock	161	139	102	79
General characteristics of charge	Highly paraffinic	Medium paraffinic	Medium aromatic	Highly aromatic
Knock rating, as per cent iso-octane in <i>n</i> -heptane	72.6	75.3	85.0	86.2

(8) Because of the oversupply of crude oil, hydrogenation in its present state of development may be considered as supplementary to present refining methods. It probably will supplant them as the supply of crude oil and demand for light products approach a balance.

Acknowledgment

The authors wish to take this opportunity of acknowledging their indebtedness to many of their associates, but particularly to the entire staff of the high-pressure research laboratory at Baton Rouge, especially W. C. Asbury, M. W. Boyer, P. J. Byrne, Jr., G. H. B. Davis, W. V. Hanks, and J. M. Jennings; and to E. M. Clark, president, and F. A. Howard, vice president, of the Standard Oil Development Company.

Since the original research and development of high-pressure hydrogenation of coal and oil has been one of the most, if not the most, costly process developments ever undertaken, the authors wish to express their respect for and admiration of the two corporations most directly responsible, the I. G. Farbenindustrie, A.-G., and the Standard Oil Company (New Jersey), and their respective presidents, Carl Bosch and W. C. Teagle.

Reactions That Occur on a Methanol Catalyst¹

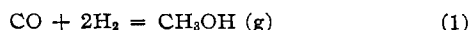
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It has been shown that carbon dioxide and hydrogen react upon a zinc oxide-chromium oxide catalyst at 304° C. to form methanol, carbon monoxide, and water. Likewise carbon monoxide and water react to form carbon dioxide and hydrogen and equilibrium can be closely approached in the water-gas reaction. Of the reactions that may occur through the action of this catalyst at

304° C. upon hydrogen-carbon dioxide-water mixtures, it has not been found possible to determine which reaction comes nearest to equilibrium. As most known methanol catalysts produce carbon dioxide or water or both along with methanol, it is possible that the formation of methanol from carbon monoxide and hydrogen may not be direct, especially as a steady state is approached.

THE thermodynamic properties of methanol have been the subject of considerable investigation. The results obtained by a number of investigators (4, 5, 7) on equilibrium in the reaction



agree as to order of magnitude. But these results differ considerably from those calculated from low-temperature

heat-capacity measurements on methanol by use of the third law of thermodynamics (3). No satisfactory explanation of this discrepancy has yet been furnished although a number of suggestions have been made (1, 4, 8).

Certain phases of the earlier work (7) led us to investigate an aspect of the problem which has not received attention aside from the mention made by Smith and Branting (7, footnote 15) in their preliminary experiments. If, as an equilibrium condition is approached in one reaction, other reactions are taking place at rates comparable with that of the reaction in question, equilibrium may not be

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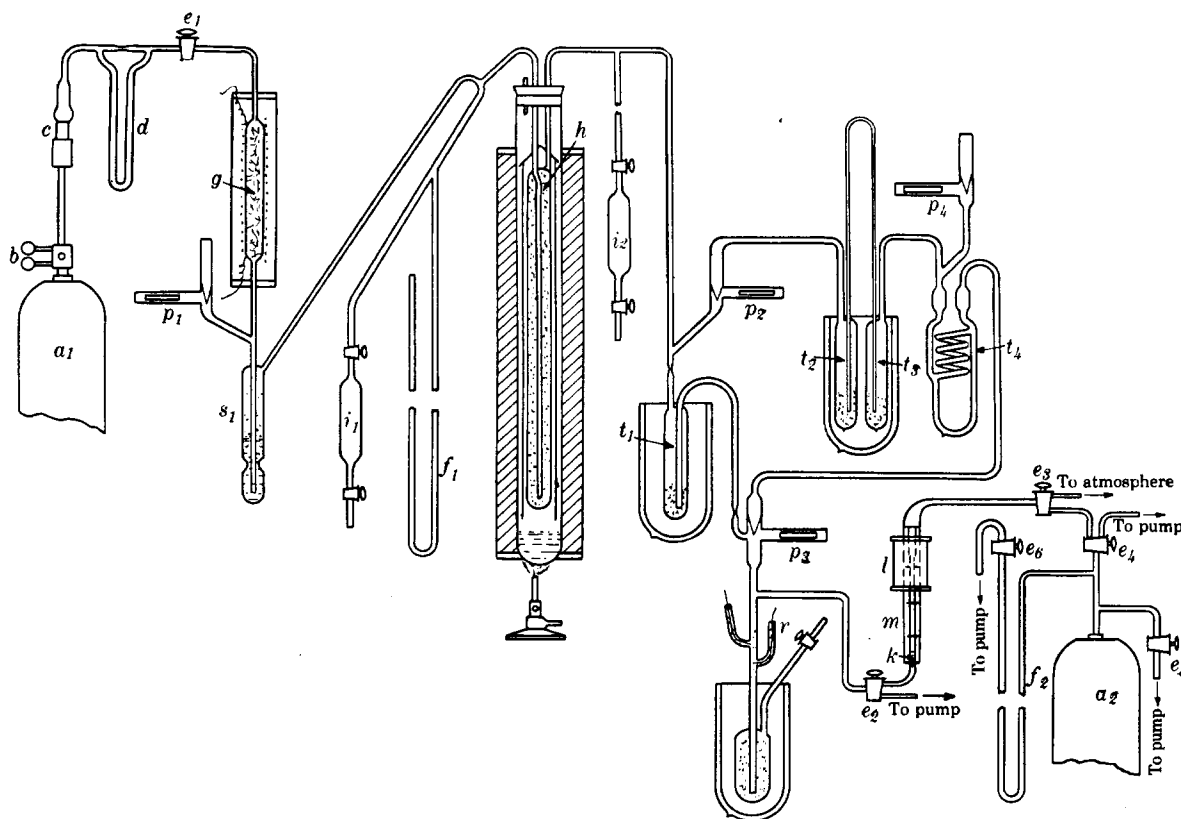


Figure 1—Apparatus Used in Experiments with Hydrogen and Carbon Dioxide at Atmospheric Pressure

readily reached. The object of the work described herein was to determine whether such a condition existed in the case of measurements thus far made of the methanol equilibrium.

It is known that, depending upon the experimental conditions, dimethyl ether, higher alcohols, methane, carbon dioxide, or water may accompany the formation of methanol from carbon monoxide and hydrogen. However, these products usually occur in amounts minor to that of the methanol. The natural assumption is, therefore, that the approach to equilibrium in the methanol reaction would not be appreciably affected by these reactions. But this need not be the case, particularly if the mechanism of the reaction by which methanol is produced is not simply that indicated by Equation 1.

EXPERIMENTAL WORK

The catalysts used in the following work were prepared by adding chromic acid solution to purified zinc oxide. The atomic proportions were about 4 Zn to 1 Cr. All of the following work was done at 304° C. on 600 cc. of catalyst.

At first several experiments were made essentially as described by Smith and Branting, but with some improvements. The total volume of gas passed over the catalyst was measured by exhausting the off-gas through an electrically operated pressure regulator into an evacuated cylinder whose volume was carefully determined and to which was attached a thermometer and a manometer for determining the amount of gas within the cylinder; also, the colorimetric method of determining the methanol was carefully investigated. By checking against known solutions of pure methanol it was found, as stated by Smith and Branting, that accurate results could be obtained only when the unknown solution was very close in concentration to the known solution with which it was compared. Some of the data reported in the preliminary experiments of Smith and Branting may be in

error on this score. Lacy, Dunning, and Storch (4) suggested that a small amount of organic product might have passed into the apparatus and vitiated the methanol determination. But the entering gas was purified by remaining in a liquid-air trap for from 30 to 60 minutes and, in the present work, the catalyst, while hot, was thoroughly evacuated with a mercury diffusion pump.

Experiments with this improved apparatus gave results in which the variations were more than seemed to be accounted for by the limits of error of the method, and the apparent nearness of approach to equilibrium did not correspond to what would be expected from the rates of gas flow used in different experiments.

Reaction upon ZnO-Cr₂O₃ Catalyst

As the reaction of carbon dioxide and hydrogen to form methanol and water was known to take place on a catalyst very similar to the one we were using, we were led to investigate this reaction upon our catalyst. A mixture of carbon dioxide and hydrogen was made from commercial carbon dioxide and electrolytic hydrogen. After passing over hot platinized asbestos, the mixture analyzed 24 per cent CO₂, 74 per cent H₂, and 2 per cent N₂. This gas mixture was passed over the catalyst at about the space velocity used in previous equilibrium experiments with carbon monoxide-hydrogen mixtures. After passage over the catalyst the methanol was removed by passage through two efficient water wash coils at 0° C. The gas then passed through the pressure regulator and into the calibrated cylinder. The first wash coil recovered 0.00095 gram of methanol. No detectable amount of methanol was found in the second wash coil. The off-gas analyzed 14.1 per cent CO₂, 69 per cent H₂, and 12.3 per cent CO. From these data, the total pressure and the total amount of gas collected in the calibrated cylinder, the constant CH₃OH/CO(H₂)² was calculated to be 3.68×10^{-4} . This value is comparable

with those obtained using carbon monoxide-hydrogen mixtures, in spite of the fact that in this case reactions other than those that produce methanol have taken place to a large extent.

This result suggested that the water-gas reaction might be occurring on the catalyst. Accordingly, pure carbon monoxide saturated with the vapor from water at 76.5° C. was passed over the catalyst. The off-gas analyzed 33 per cent CO₂, 33 per cent CO, and 31 per cent H₂. Experiments at 300° C. and at 50 and 200 atmospheres with gas mixtures containing 60 per cent CO and 40 per cent H₂O showed that the water-gas reaction still took place at a rate comparable with that at which methanol is formed from carbon monoxide and hydrogen, although large concentrations of water vapor in the gas at temperatures as low as 300° C. caused a rather rapid deterioration in the activity of the catalyst—probably accompanying hydration of the chromium oxide. Considerable methanol was obtained from the carbon monoxide-water mixture upon some catalysts tried.

Further Study of Reactions and Determination of Equilibrium

It was thought of interest to study in greater detail the reaction between hydrogen and carbon dioxide using the original catalyst and determining the partial pressure of water in the equilibrium mixtures. The apparatus shown in Figure 1 was used. The storage cylinder, *a*, contained the hydrogen-carbon dioxide mixture and was connected to the apparatus through the copper-to-glass seal, *c*. The gas from the cylinder passed through a high grade reducing valve, *b*, by means of which the rate of gas flow, as indicated by the flowmeter, *d*, was controlled. A tube, *g*, containing platinized asbestos, removed oxygen from the gas, and a magnetically operated device, *p*, introduced water to the saturator, *s*₁, kept at a constant temperature of 20° C. The tubing between *s*₁, *i*₁, *f*₁, and *h* was 1.5 mm. in internal diameter and was heated by resistance wire to prevent condensation of water vapor from the saturator. The catalyst, *h*, was surrounded by a thin metal "umbrella" and heated by the vapor of boiling benzophenone. After thorough evacuation of the heated catalyst with a mercury diffusion pump, the gas was introduced to the apparatus and the saturator, *s*₁, was filled with water by operating the slug, *p*₁. The gas was passed through the apparatus for several days in order to bring the catalyst into equilibrium with the H₂-CO₂-H₂O mixture. During this period the gas passed through the trap, *t*₁, through the electrically operated pressure regulator, *r*, and to the atmosphere. Then *t*₁ was sealed off and the glass tips at *p*₂ and *p*₃ were broken by the slugs. The gas now passed through the traps *t*₂ and *t*₃, cooled in acetone-carbon dioxide snow, and a weighed

which was known and in which the gas pressure could be measured. Condensation of water was prevented by electrically heating the tubing from *h* to *i*₂. The water passing out in the gas was determined by sealing off and weighing the trap, *t*₂, after displacing the gas with dry air. The water in *t*₄ was added to *t*₂ after it was again cooled in acetone-carbon dioxide snow. The methanol was determined in the uniform solution.

The data obtained in four experiments are recorded in Table I. The gas used in these experiments originally analyzed 24 per cent CO₂, 74 per cent H₂, and 2 per cent N₂ after passage over the platinized asbestos. This gas was saturated with the vapor from water held at 20° C.

Table I—"Equilibrium" in System H₂-CO₂-CO-H₂O-CH₃OH at 304° C.

EXPT.	GAS FLOW RATE	CH ₃ OH	H ₂ O	COMPOSITION OF OFF-GAS			TOTAL PRESSURE	VOLUME OFF-GAS AT S. T. P.
				CO ₂	H ₂	CO		
	Liters per hour	Gram	Grams	%	%	%	Mm. Hg.	Liters
1	0.6	0.0008	1.95	20.0	66.0	13.2	800	41.0
2	0.8	0.0006	1.87	27.2	64.6	5.1	817	34.9
3	0.33	0.00024	1.97	25.6	67.3	5.2	813	30.5
4	0.93	0.00030	1.03	25.5	66.1	4.8	817	30.9

The data in Table II are calculated from those given in Table I. They show equilibrium constants and corresponding values of the free-energy change for four possible reactions. The values of $\Delta F_{\text{CH}_3\text{OH}}$ are calculated from the corresponding ΔF and Eastman's (2) values for the free energies of carbon monoxide, carbon dioxide, and water.

It was hoped in this series of experiments to determine which of these possible reactions came nearest to equilibrium at the different rates of gas flow. This purpose was probably defeated by uncontrollable changes in activity of the catalyst. However, examination of the data recorded in Table II, together with the facts presented above, shows the inconsistency of picking out any one reaction involving methanol (for example, the hydrogen-carbon monoxide reaction) as the one in which the methanol is nearest to equilibrium. The writers believe that the data presented here indicate that side reactions may under certain conditions introduce some error into measurements of the methanol equilibrium.

Note—Recently Walther A. Roth of Germany has given, in a personal communication, a brief account of results he has obtained in a redetermination of the heat of combustion of methanol. He finds the heat of combustion of liquid methanol to be 173,300 calories per gram-molecule at constant pressure and (presumably) 18° C. He considers the earlier data by Richards and Davis (6) to be in error due to the presence of water in their sample of methanol. Using the specific-heat data given by Kelley (3), the free energy

Table II—"Equilibrium" in Four Possible Reactions at 304° C.

RUN	2H ₂ + CO = CH ₃ OH			3CO + 2H ₂ O = CH ₃ OH + 2CO ₂			CO ₂ + 3H ₂ = CH ₃ OH + H ₂ O			CO + H ₂ O = H ₂ + CO ₂	
	K	ΔF	$\Delta F^\circ_{\text{CH}_3\text{OH}}$	K	ΔF	$\Delta F^\circ_{\text{CH}_3\text{OH}}$	K	ΔF	$\Delta F^\circ_{\text{CH}_3\text{OH}}$	K	ΔF
1	3.8×10^{-4}	+9037	-28,886	6.8×10^{-1}	+437	-29,447	8.9×10^{-4}	+13,345	-28,597	42	-4300
2	6.7×10^{-4}	+8390	-29,533	17.0×10^{-1}	-595	-30,480	13.0×10^{-4}	+12,897	-29,045	50	-4498
3	2.4×10^{-4}	+9300	-28,623	4.2×10^{-1}	+995	-28,890	5.7×10^{-4}	+13,857	-28,085	41	-4264
4	3.67×10^{-4}	+9078	-28,845	24.8×10^{-1}	-1043	-30,928	4.5×10^{-4}	+14,128	-27,814	80	-5029

amount of water was introduced to the wash coil, *t*₄, by operating the slug, *p*₄. Methanol and water were condensed in the traps *t*₂ and *t*₃, and the last traces of methanol were removed by the water in *t*₄ kept at 0° C. However, as no methanol or water was found in the second trap, it was later eliminated. The off-gas then passed through the magnetically operated valve, *l*, into the cylinder, *a*₂, the volume of

of CO given by Eastman (2) and this new value of the heat of combustion of methanol, the equation for the free-energy change in Reaction 1 is $\Delta F = -18,050 + 45.00 T \log_{10} T - 0.01586 T^2 - 69.4 T$. The equilibrium constant calculated from this equation for 304° C. is 7.4×10^{-4} . This is in very satisfactory agreement with the value 5.6×10^{-4} experimentally determined by Smith and Branting (1). This equation combined with the value for the free energy of carbon monoxide as given by Eastman (2) gives -29,590 calories for the free-energy of CH₃OH(g) at 304° C., which may be compared with the data in Table II.

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.

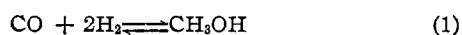
The experimental investigations agree only as to order of magnitude, the disagreement being as much as several hundred per cent. Only a small part of this discrepancy can be accounted for by the effect of pressure on K_p . This is treated in detail in the paper and values of K_{p_0} (equilibrium constant 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.

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:



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.

¹ Received August 29, 1930.

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

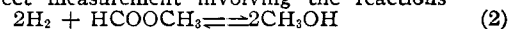
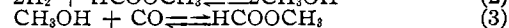
³ Present address, Roessler and Hasslacher Chemical Co., Perth Amboy, N. J.

Previous Work

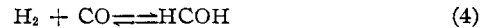
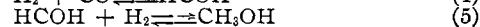
There have been three main avenues of attack on this problem:

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

(2) Indirect measurement involving the reactions



or the reactions



(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 ΔF° 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