[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, YALE UNIVERSITY]

The Equilibrium between Carbon Monoxide, Hydrogen, Formaldehyde and Methanol.[1] I. The Reactions $CO + H_2 \rightleftharpoons HCOH$ and $H_2 + HCOH \rightleftharpoons CH_3OH$

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Introduction

Because of its great industrial importance the direct synthesis of formaldehyde from carbon monoxide and hydrogen has attracted the attention of investigators for many years. (All investigations in which synthesis was attempted in the presence of special forms of energy such as electrical discharges, or ultraviolet radiation, are beyond the scope of this paper; only the purely thermal synthesis will be considered.) In spite of all the attempts that have been made to bring about this reaction there appear to be no quantitative results of any value and there is not even a qualitative agreement on the possibility of the synthesis. The successful accomplishment of the methanol synthesis at high pressures has aroused new interest in the problem. In the published investigations of the methanol synthesis there has been practically no mention of formaldehyde and only one paper giving any data. Several recent patents claim good yields of formaldehyde in high pressure synthesis from carbon monoxide and hydrogen but the claims are not supported by any experimental facts.

The failure of most investigators to obtain more than a trace of formaldehyde (and even that doubtful in most cases) may be due either to an unfavorable equilibrium or to lack of the proper catalyst. Some recent investigators[2] have inclined to the latter view, but the preponderance of evidence points to a very unfavorable equilibrium.

There are no low temperature thermal data on formaldehyde and so the third law of thermodynamics cannot be applied to the calculation of an equilibrium constant. Parks and Huffman[3] have recently presented an equation for the free energy of formation of formaldehyde, based on a rough analogy between the structure of formaldehyde and ethylene. Combining this with their value for the free energy of carbon monoxide, the value of Kp for the formaldehyde synthesis reaction may be calculated. A value of 5×10^{-6} is obtained at 250°. The Nernst approximation, which is often surprisingly accurate, also predicts a very small equilibrium constant for this reaction but this prediction is rather uncertain because of the conflicting data on the heat of combustion of monomolecular formal-

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(1) This paper is based on a Dissertation presented by R. H. Newton in June, 1933, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. It is also a revision of a preliminary paper presented before the Division of Physical and Inorganic Chemistry at the Denver meeting, August, 1932.

(2) Bone, *Trans. Inst. Chem. Engrs.* (London), **8**, 98 (1930); Frolich, *Ind. Eng. Chem.*, **23**, 111 (1931).

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

dehyde gas. Using the heat of combustion of formaldehyde gas determined by von Wartenburg and Lerner-Steinberg[4] ($\Delta H = -134{,}700$) and other recent thermal data, the predicted value of the equilibrium constant at 250° is 0.5×10^{-6}. It is to be noted that small errors in the heat of combustion of formaldehyde will make a very large error in the calculated Kp because the heat of reaction is less than one-hundredth of the heat of combustion. Hence it is necessary to make actual equilibrium measurements if anything approaching a trustworthy value for Kp is to be obtained.

The reaction $CH_3OH \rightleftharpoons HCOH + H_2$ is the basis of the commercial process for formaldehyde manufacture and yet there are no reliable data on the equilibrium conditions. It is also to be noted that a combination of this reaction with the methanol synthesis reaction, for which fairly reliable equilibrium data exist, enables one to secure a check on the directly-determined value for the equilibrium constant of the formaldehyde synthesis reaction.

It is the belief of the authors that this paper presents the first reliable experimental data on the equilibrium conditions in those two reactions.

Review of Previous Work

Synthesis of Formaldehyde.—A number of investigators[5] have attempted to synthesize formaldehyde over catalysts at atmospheric and slightly elevated pressures. The results are conflicting but the general conclusion is that either a very slight trace of formaldehyde or none at all results when carbon monoxide and hydrogen are passed over a catalyst.

Formaldehyde has not been reported in most of the high pressure synthesis from carbon monoxide and hydrogen but Morgan, Hardy and Proctor,[6] have definitely identified formaldehyde in the products resulting from the reaction of carbon monoxide and hydrogen at high pressure over Cr–Mn–Rb catalysts. Only 0.2% of the total carbon reacting appeared as formaldehyde at a temperature of 420° and a pressure of 200 atm.

It should be noted that many of the above-mentioned investigators were quite vague as to their methods of determining formaldehyde and none of them can be said to have obtained quantitative results for the equilibrium.

Decomposition of Formaldehyde.—There has been a vast amount of work on this subject. The conclusion reached by a number of the later investigators,[7] is that formaldehyde is almost completely decomposed at 1 atm. and at all temperatures above 150°. Ghosh and Chakravarty,

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(4) Von Wartenburg and Lerner-Steinberg, *Z. angew. Chem.*, **38**, 591 (1925).

(5) Jahn, *Ber.*, **22**, 989 (1889); Chapman and Holt, *J. Chem. Soc.*, **87**, 916 (1905); Gautier, *Compt. rend.*, **150**, 1564 (1910); Marshall and Stedman, *Trans. Roy. Soc. Can.*, [III] **17**, 53 (1923); Jaeger and Winkelmann, *Ges. Abhandl. Kenntnis Kohle*, **7**, 55 (1925); Sabalitschka and Harnisch, *Biochem. Z.*, **190**, 265 (1927); Neumann and Biljcevic, *Z. angew. Chem.*, **40**, 1469 (1927); Vogel, *Helv. Chim. Acta*, **11**, 370 (1928); Fischer and Jaeger, *Ges. Abhandl. Kenntnis Kohle*, **7**, 68 (1925).

(6) Morgan, Hardy and Proctor, *J. Soc. Chem. Ind.*, **51**, 1T (1932).

(7) Tropsch and Roelen, *Ges. Abhandl. Kenntnis Kohle*, **7**, 15 (1925); Marshall and Stedman, *loc. cit.*; Ghosh and Chakravarty, *Quart. J. Indian Chem. Soc.*, **2**, 142 (1925); Medvedev and Robinson, *Trans. Karpov. Chem. Inst.*, **3**, 54 (1924).

however, find Kp to be greater than 1.0 at all temperatures below 300° and it appears that their results are not above suspicion.

The Dehydrogenation of Methanol.—This has also been the subject of many investigations, and the results are conflicting. The interpretation of much of this work given by textbooks[8] is vague, particularly as regards temperature. The implication is that methanol may be appreciably dehydrogenated to formaldehyde at temperatures below 300°. Ghosh and Baksi reported almost complete conversion of methanol to formaldehyde at 200°[9] but this is at variance with nearly all other workers in this field.

The commercial process for manufacture of formaldehyde from methanol is essentially a dehydrogenation since an insufficiency of oxygen is used, but it is well known that temperatures above 400° and high space velocities are necessary for good yields. The data reported by LeBlanc and Plaschke[10] might enable one to estimate very roughly the equilibrium constant of the reaction.

Apparently the reverse reaction or hydrogenation of formaldehyde had not been studied quantitatively. Sabatier[8] states that it takes place readily over nickel even at as low a temperature as 90°. Fischer[11] refers briefly to experiments in which $H_2 + HCOH$ yielded considerable quantities of methanol at 400° and 100 atm.

Experimental Part

Analytical Methods.—Gas analyses were made on a U. S. Steel Corporation type of Orsat gas analysis apparatus provided with a mercury-sealed buret and a compensator for temperature and pressure changes. The percentage of illuminants was found to be negligible so the analysis was simplified by omitting this step. Carbon monoxide was determined by absorption in acid cuprous chloride, methane and hydrogen by slow combustion with a platinum spiral.

In the experiments on the hydrogenation of formaldehyde, the liquid product was analyzed for formaldehyde, methanol and methyl formate. Methyl formate was determined by saponification, the details of the method being worked out by a series of experiments on known amounts of pure methyl formate. Methanol and formaldehyde were found not to interfere with this determination. Methanol was determined by the method of Lockemann and Croner,[12] which is total oxidation with alkaline permanganate with subsequent correction for the amounts of formaldehyde and methyl formate found. The methyl formate equivalent of 1 cc. of 0.5 N permanganate was found to be the theoretical value of 0.00375 g. of methyl formate per cc. of permanganate used. In the case of formaldehyde, the theoretical equivalent was used. Formaldehyde was determined by the iodine method of Romijn.[13] According to the literature, methanol and methyl formate do not interfere, and this was found to be true as long as one was not

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[8] Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922; Rideal and Taylor, "Catalysis in Theory and Practice," The Macmillan Co., New York, 1926; Hilditch, "Catalytic Processes in Applied Chemistry," D. Van Nostrand Co., New York, 1929.

[9] Ghosh and Baksi, *Quart. J. Indian Chem. Soc.*, **3**, 415 (1926).

[10] LeBlanc and Plaschke, *Z. Electrochem.*, **17**, 45 (1911).

[11] Fischer and Tropsch, *Ber.*, **56**, 2438 (1923).

[12] Lockemann and Croner, *Z. anal. Chem.*, **54**, 11 (1915).

[13] Romijn, *ibid.*, **36**, 18 (1897).

attempting to determine extremely small amounts of formaldehyde. Acetone, however, does interfere, but at concentrations above one part in 250,000 there is an opalescence due to iodoform, even in the presence of 10% methanol which was the maximum amount present in any of the solutions analyzed. An opalescence was not observed and so the absence of acetone was assumed. The methods were tested on the pure substances and on mixtures of all three and found to be accurate to about 2%.

In the experiments on direct synthesis of formaldehyde and methanol the amount of condensate was very much smaller and a more sensitive method for formaldehyde was necessary. It was found that by using *n*/100 iodine, the Romijn method could be made much more sensitive without appreciable loss in accuracy. In pure formaldehyde solutions, or in mixtures of formaldehyde and methyl formate, an accuracy of 2% could be obtained in solutions which contained only 0.20 mg. of formaldehyde. This method was found to be more sensitive than any of the colorimetric methods, since it was less affected by dilution. An extensive survey of the colorimetric tests for formaldehyde was made, and the morphine test of Bonnet[14] and the well-known Schiff's test were found the most sensitive and the most specific. Most of these tests are not suitable for quantitative determination since the colors are so readily affected by slight changes in conditions. Thus the morphine test was used qualitatively only, since the color was somewhat modified by the presence of methanol. The Schiff test was applied quantitatively, as it appeared to be unaffected by methanol or methyl formate, but it is somewhat less sensitive than the morphine test. Substances other than formaldehyde give a color, but a blue color appears to be specific.

Since very small amounts of formaldehyde had to be determined in the presence of relatively large amounts of methanol, it was necessary to examine carefully the question of interference by methanol. A large number of tests were made on methanol purified from traces of aldehydes by distillation from alkaline iodine solution, and from silver oxide and it was definitely established that 0.01 *N* iodine does react with methanol, the extent of reaction being a function of time and iodine concentration. By reducing the time to the minimum found necessary for complete reaction with formaldehyde (15 minutes) and using only a small excess of iodine solution (about 10%), the percentage error was minimized. The following tabulation, giving results on the analysis of known mixtures, shows the extent of the interference.

TABLE I

INTERFERENCE OF METHANOL WITH THE 0.01 *N* IODINE METHOD FOR FORMALDEHYDE

MeOH taken, g.	0.16	0.16	0.16	0.32	0.32	0.32	0.64	0.64	0.64
HCHO taken, mg.	.00	.81	1.61	.00	.81	1.61	.00	.81	1.61
HCHO found, mg.	.10	.83	1.66	.09	.86	1.68	.18	.88	1.72
Error, mg.	.10	.02	.05	.09	.05	0.07	.18	.07	0.11

It is evident that the error is less than 10% when the amount of formaldehyde is 1.0 mg. or more, and in most cases the solution analyzed contained more formaldehyde than this. Furthermore, these results were obtained using 50–100% excess iodine and in the analysis of actual condensates a smaller excess was used. The thiosulfate equivalent of the iodine solution was checked frequently. The formaldehyde determination was also checked by the colorimetric method using Schiff's reagent by comparison with solutions of known formaldehyde content. Since the formaldehyde concentration was so small in most cases that several hours were generally required to develop the color, this method was not very accurate. On the other hand, it appears to be fairly specific, whereas a good many substances might conceivably interfere with the iodine method. In the majority of the runs, the iodine method gave higher results than the colorimetric

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[14] Bonnet, THIS JOURNAL, **27**, 601 (1905).

which indicated the presence of some interfering substance. In one run (No. 84) in which the largest amount of product was obtained, the iodine method gave a definite precipitate which appeared to be iodoform. When correction was applied for the amount of iodoform obtained, the two methods checked quite well. In all the runs the two methods checked fairly well when one considers the very small amounts of formaldehyde present and this agreement is considered to be definite proof that formaldehyde was actually synthesized. In calculating equilibrium constants, the results of the colorimetric method were used.

Methanol was also determined by two methods, the oxidation method previously referred to and the colorimetric method developed by Smith and Branting from the methanol test of Wright.[15] If the latter method was carried out with great care, the two methods were found, by tests on known solutions, to agree within 10% even when only a few milligrams of methanol were present. In the actual analysis of condensates, the agreement was much better than this.

Consideration was given to several other substances which might, if present, interfere with the formaldehyde or methanol determination. Dimethyl ether has been shown by Dodge[16] to interfere with the colorimetric determination of methanol, and presumably it would also interfere with the oxidation method. Since no dehydrating catalysts were used in any of the final equilibrium runs, no dimethyl ether would be expected, but the following test was made to settle this point more definitely. Formaldehyde was hydrogenated at a temperature of 250° using the same catalyst that was used in the final equilibrium measurements. About 10 cc. of condensate was collected and, of this, 2 cc. was distilled into concentrated sulfuric acid, which was kept cold by a water-bath. Upon dilution of the acid and heating to 80°, no gas was set free. According to Erlenmeyer and Kriechbaumer[17] the solubility of dimethyl ether in cold sulfuric acid and its release on dilution and warming is characteristic (confirmed by McKee and Burke),[18] so the fact that no gas was given off was taken as evidence of the absence of dimethyl ether.

Methylal, which might possibly be formed, was found to interfere with the colorimetric determination of formaldehyde, but the color was crimson instead of the characteristic blue of formaldehyde. However, the interference with the iodine test was shown to be extremely small, so that a quantity of methylal sufficient to give a deep crimson color test would not interfere with the iodine method. From the fact that the Schiff's reagent color was always blue, and that the colorimetric and iodine methods for formaldehyde checked about as well as could be expected, it is concluded that methylal was not present in sufficient amount to affect either the formaldehyde or methanol determinations.

Catalysts.—In the study of the hydrogenation of formaldehyde, various catalysts were used in an attempt to obtain a clean-cut reaction. In the synthesis runs with hydrogen and carbon monoxide as starting materials only copper–zinc catalysts were used since previous work in this Laboratory had shown them to be the most active methanol catalysts. With the exception of the platinum and osmium catalysts, the procedures for their preparation were practically identical. All chemicals used were of the C. P. grade. The usual starting material was the metal or its oxide, which was dissolved in nitric acid and diluted to a concentration of 15 g. of metal per liter. Chromic nitrate, however, was prepared by the reduction of potassium dichromate with ethyl alcohol. The solutions were mixed to get the proper molal proportions and heated to the precipitation temperature. The precipitant was then added with stirring. The catalysts were then washed by decantation five or more times and filtered on a Buchner

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(15) Smith and Branting, THIS JOURNAL, **51**, 129 (1929); Wright, *Ind. Eng. Chem.*, **15**, 788 (1923).

(16) Dodge, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 23 (1932).

(17) Erlenmeyer and Kriechbaumer, *Ber.*, **7**, 699 (1874).

(18) McKee and Burke, *Ind. Eng. Chem.*, **15**, 788 (1923).

funnel. Some needed only to be dried at 105° and crushed to pass 8 mesh, the portion held on 16 mesh being used. Others were pressed in a hydraulic press to make a more dense cake and then dried and crushed. Some were so soft that they were formed into small pills in a pill machine usually with the aid of a few per cent. of graphite as binder. Table II gives the important facts concerning the catalysts used.

TABLE II

DATA FOR THE PREPARATION OF CATALYSTS

Catalyst	Molal composition[a]	Precipitant	Temp. of precipitation, °C.	Method of forming granules
1 and 1a	$CuZn_3$	Satd. Na_2CO_3	Room	Moist filter cake pressed
2 and 2a	Cu	30% NaOH	80	Dried and crushed without other treatment
3	Ni	30% Na_2CO_3	80	
4 and 4a	$Cu_{19}Zn$	30% Na_2CO_3	80	Pilled with 3% graphite
5	$Cu_{99}Ce$	30% Na_2CO_3	80	Pilled with 2% graphite
5a	$Cu_{99}Ce$	30% Na_2CO_3	80	Moist filter cake pressed
6	$Ni_{99}Ce$	30% Na_2CO_3	80	Dried and crushed without other treatment
7	$Cu_{19}Cr$	30% Na_2CO_3	80	Moist filter cake pressed
8 and 8a	Zn	30% Na_2CO_3	Room	Dried and crushed without other treatment
9	Os	Concd. NH_4OH	Room	Precipitated on acid-washed pumice
10	Pt	Alkaline formalin	Room	
11, 11a, 11b	$CuZn_2$	30% Na_2CO_3	Room	Moist filter cake pressed
11	$CuZn_2$	30% Na_2CO_3	Room	Pilled without binder
12	$CuZn_3$	30% Na_2CO_3	Room	Moist filter cake pressed
13	Zn_9Cr_{11}	Satd. Na_2CO_3	...	Dried and crushed without other treatment

[a] Determined from the weights of metals used.

Extreme care was taken with the preparation of No. 12 to ensure the absence of alkali in the finished catalyst. Besides using a deficiency of sodium carbonate, it was washed fifteen times by decantation.

The catalysts were reduced in place in the reactor, a mixture of two parts of hydrogen and one of carbon monoxide being used for all except the platinum and osmium ones, for which pure hydrogen was used. A slow stream of gas was maintained and the furnace allowed to heat up slowly to about 200° in the course of twenty-four hours, and then the temperature was held at this point for another twenty-four hours. The pure zinc catalyst was further activated at a temperature of 435° as it was found very inactive after the low temperature treatment.

Apparatus and Procedure.—The hydrogenation of formaldehyde and the reverse reaction were studied at atmospheric pressure and the formaldehyde synthesis reaction at three atmospheres. A few preliminary runs on formaldehyde synthesis at atmospheric pressure showed that a higher pressure was desirable in order to secure enough product to measure with even rough precision. Too high a pressure is undesirable because the ratio of methanol to formaldehyde in the product increases with pressure.

The investigation of formaldehyde hydrogenation necessitated a means of producing a mixture of hydrogen and formaldehyde vapor, preferably of definite and constant composition, and considerable work was done on this preliminary problem. The use of liquid formaldehyde, made by condensing the monomolecular vapor, according to the method of Trautz and Ufer was thought to offer a possible solution,[19] but it was found that the liquid so produced was not entirely dry even after several fractionations, so

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(19) Trautz and Ufer, *J. prakt. Chem.*, **113**, 105 (1926).

that when a portion had been evaporated the residue polymerized very rapidly. It was evident that this method would not enable one readily to obtain the relatively large amounts of formaldehyde vapor needed and hence it was abandoned. An attempt was made to dry the formaldehyde vapor by a number of desiccants such as phosphorus pentoxide, calcium chloride and anhydrone, but it was found that these reagents absorbed the formaldehyde without drying it, and in the case of phosphorus pentoxide the formaldehyde was actually decomposed. A number of experiments were made to determine whether the concentration of formaldehyde gas would be definite if hydrogen were passed over paraformaldehyde heated to a constant temperature. It was found that the concentration depended on the previous history of the paraformaldehyde as well as the temperature, since it decreased continually as the paraformaldehyde was evaporated. None of the other formaldehyde polymers appeared to offer any better solution to the problem. Inasmuch as this appeared to be the only practicable method, it was finally adopted, although it meant that a steady state was not attained and material balances could not be made.

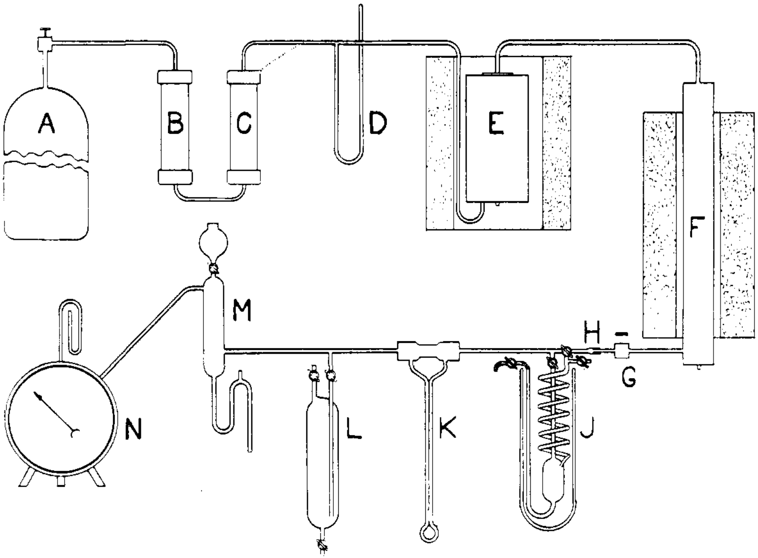

Fig. 1.—Arrangement of apparatus.

Essentially the same apparatus, with minor changes in details, was used for the study of both reactions. Referring to Fig. 1, the gas (hydrogen in the case of the hydrogenation and dehydrogenation reactions and a mixture of carbon monoxide and hydrogen for the synthesis reaction), stored in a steel cylinder A under a pressure of about 135 atm., was withdrawn through the usual diaphragm reducing valve, and passed through copper tubing into tube B (made of a 15 cm. length of standard $1^1/_4''$ (3.18 cm.) pipe, fitted with caps), containing a layer of silica gel 13 mm. deep to remove entrained oil, and a layer of Ascarite 12.5 cm. deep to remove carbon dioxide. Tube C, exactly similar to B, was filled with activated silica gel to remove any methanol or other condensable vapors from the gas and to dry it. D is a mercury manometer 2 meters high on which the total pressure of the system was measured. The formaldehyde saturator E, used only when hydrogenation of formaldehyde was under investigation, was made from 4″ (10.2 cm.) brass tubing, 20.3 cm. long, with soldered brass heads. The top head had a 5.08 cm. hole for filling, closed by a brass cover, secured by studs and rendered gas-tight by an asbestos gasket. The saturator held about 700 g. of paraformaldehyde in the form of small pills. The temperature of the saturator was measured by a thermometer inserted in a well in the bottom. An electric furnace fitted over the saturator for heating to the desired temperature. The methanol saturator, used when the dehydrogenation reaction was studied, was interchangeable with that for formaldehyde, and was of similar construction but much smaller. For investigation of formaldehyde synthesis starting from carbon monoxide and hydrogen the saturators were omitted altogether and were replaced by a short piece of copper tubing. From E the gas passed through a tube, which was electrically heated to prevent condensation of the methanol or polymerization of the formaldehyde, to the reactor F, which is shown in detail in Fig. 2. This was constructed of 2″ (5.08 cm.) copper tubing, 25.4 cm. long, fitted with soldered brass heads, into which screwed brass plugs, aluminum gaskets being used for gas-tight connections. The catalyst bed was 15.2 cm. deep and was located in the exact center of an electric tube furnace. The ends of the reactor which projected beyond the furnace were well lagged with magnesia. This reactor had a capacity of 300 cc. of catalyst. A smaller reactor of similar design with a capacity of 30 cc. of catalyst and interchangeable with the larger one was used in some of the runs.

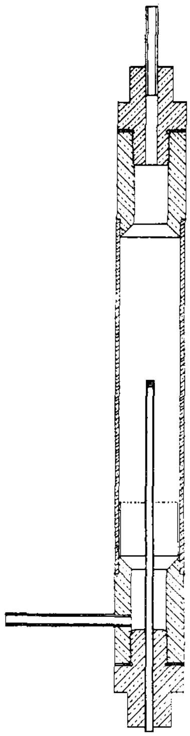

Fig. 2.—The catalyst reactor.

The temperature of the catalyst bed was measured by a calibrated thermocouple inserted in a well located in the center of the catalyst bed. A brass needle valve G was used to adjust the flow of gas to the desired value.

Up to G the apparatus was all metal, beyond it all glass, the connection being made by means of a copper–Pyrex seal at H. This was rather fragile, but otherwise gave satisfactory results. Two types of condensers were used, the type shown in the figure when a large amount of condensate was expected as in the case of hydrogenation and a plain "U" tube for smaller amounts as in the case of formaldehyde synthesis. The coil type could be used only with solid carbon dioxide as a refrigerant since the coils plugged if the temperature were low enough to freeze the methanol. The "U" type was used with liquid air as a cooling medium to ensure complete condensation of the very small amounts of formaldehyde and methanol produced. It also had the advantage of being small enough so that it could be weighed on an analytical balance, thus obtaining the weight of condensate as a check on the analytical results. Constant flow of gas was indicated by means of the flowmeter K. A gas sample was taken as nearly continuously as possible, with the sampler L, which was designed to give a constant rate of sampling. The gas was finally saturated with water in the saturator M, and the total volume determined by the calibrated wet-test meter N.

In the experiments on the hydrogenation of formaldehyde the temperature of the catalyst was maintained manually at the desired figure. Since the reaction was strongly exothermic in most cases, and conditions not closely reproducible, it was very difficult to maintain any particular temperature. The synthesis runs starting from carbon monoxide and hydrogen were much longer, varying from 5 to 122 hours in length, and automatic temperature regulation was necessary. This was obtained by means of a relatively simple photo-electric type of controller which has been described in detail elsewhere.[20] With this apparatus, the temperature of the furnace could be controlled within 1.0° at any desired temperature regardless of fluctuations of line voltage. (In several

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[20] Newton and Furnas, *Chem. Met. Eng.*, **39**, 455 (1932).

runs the maximum variation was only ±0.1°.) A Leeds and Northrup recording potentiometer was used to check the temperature continuously while the operator was away.

The reducing valve held the pressure very constant, the variation in absolute pressure being largely due to changes in the barometer. In the runs at 3 atm. the uncertainty in the pressure was probably not more than ±0.01 atm.

Naturally the exact technique of operation varied according to the reaction being studied. In general the reactor was allowed to come up to temperature before the gas stream was started. If the paraformaldehyde saturator was being used, it was also allowed to come up to operating temperature before the gas was started. The methanol saturator was not heated, since a high enough concentration of methanol could be obtained at room temperature. During this "warm-up" period the gases were by-passed around the cold condenser to the flowmeter so that the rate of flow of gas could be set at the desired figure. Before a run the condenser was always washed out with pure methanol and dried by a stream of air sucked through it by means of a water jet pump. This was usually continued for about half an hour to ensure that no methanol was left in the condenser. When conditions had become constant, and had remained so for about fifteen minutes, the run was started by immersing the condenser in the cooling bath and cutting out the by-pass. The gas sampler was not started until a few minutes later in order to allow time for the air in the condenser to be swept out. Readings were taken at regular intervals, their frequency depending on the length of the run. It was found desirable to test the apparatus for leaks immediately before and after each run.

When liquid air was used as a cooling medium, any carbon dioxide and water formed in the reaction condensed as a solid in the upper part of the condenser and would cause stoppage of the flow if allowed to accumulate. Hence it was necessary in the longer runs to melt it out about twice a day. This was done by warming the condenser with the fingers at the point where the plug had formed and, in general, this dropped to the bottom of the "U" tube where it did no harm.

Since only very small amounts of formaldehyde and methanol were collected in the synthesis runs, it was necessary to make a blank run to be certain that the products determined actually came from reaction and not from some other source. A run of thirty-eight hours' duration was made using nitrogen gas, at a temperature of 250° and pressure of about 2 atm. and with the identical catalyst used in the final synthesis runs. No product was visible in the condenser, and no test for either methanol or formaldehyde was obtained by either of the two methods of analysis, on the liquid obtained by rinsing out the condenser with a small amount of water.

Experimental Results

Hydrogenation of Formaldehyde.—Forty-seven runs were made in the study of this reaction over the temperature range 117–237°, the majority being in the direction of hydrogenation. They are not closely reproducible for several reasons, one being the difficulty in maintaining steady conditions already mentioned, another the fact that the activity of the catalysts changes with use and finally the fact that the reaction is not clean and slight changes in conditions appear to exert considerable influence on the extent of side reactions in relation to the main reaction. The space velocities were higher than would normally be used for a close approach to equilibrium but this reaction appears to be quite rapid and nothing was gained by going to lower rates of flow because of the rapid increase in extent of side reactions.

Nine of these runs have been selected as most suitable for the calculation of an equilibrium constant. The basis for selection was mainly the fact that these runs are closely grouped about a given temperature. Due to the uncertainty of the thermal data, the effect of temperature on the equilibrium constant cannot be calculated with any degree of assurance. The results calculated from the observed data for these nine runs are presented in Table III.

TABLE III

EXPERIMENTAL RESULTS ON THE HYDROGENATION OF FORMALDEHYDE

Run[a]	Temp., °C.	Catalyst	Space velocity[b]	Distribution of carbon among products						Kp[c]
				% as CO_2	% as CH_4	% as CO	% as HCOH	% as CH_3OH	% as methyl formate	
28	200	4a	85	4.3	0.6	19.1	0.0043	73.0	3.0	2400
34^{D}	192	4b	180	1.8	.9	4.7	.25	86.8	5.6	404
35^{D}	189	4b	225	1.1	.4	4.7	.078	87.5	6.5	1740
36^{D}	191	4b	225	0.0	.0	3.2	.29	93.7	2 8	414
37	201	4b	450	1.9	.1	7.0	.15	39.9	52.8	2400
38	201	4b	425	0.8	.1	3.2	.14	29.9	68.9	3000
39	201	4b	450	0.7	.0	2.8	.26	24.0	72.3	3450
40^{D}	200	1a	380	5.9	1.8	23.9	.065	68.3	0.0	1950
42^{D}	203	8a	370	1.6	0.7	3.5	.048	94.4	.0	3080

[a] D signifies that equilibrium was approached from the dehydrogenation side.

[b] Liters of exit gas (at standard conditions) per liter of catalyst volume per hour.

[c] $Kp = Px_{\mathrm{MeOH}}/Px_{\mathrm{HCOH}}Px_{\mathrm{H_2}}$, where P is the total pressure and x is mole fraction.

The calculated values of Kp agree remarkably well when one considers the extent of the side reactions that occurred in some cases. That an approximation to the equilibrium state was reached is indicated by the agreement between hydrogenation and dehydrogenation runs. Averaging the temperature and Kp values, one obtains the result t = 197°, Kp = 2090.

TABLE IV

EXPERIMENTAL RESULTS FOR FORMALDEHYDE SYNTHESIS

Run[a]	Temp., °C.	Space velocity[b]	Press., atm.	Duration of run, hrs.	Mg. of formaldehyde		$Kp \times 10^5$
					Iodine method	Colorimetric	
50	243	11.3	3.00	25.0	0.27	0.50	0.88
51	243	17.9	2.99	46.0	2.12	1.90	2.01
52	243	7.3	3.05	45.3	1.33	0.50	0.85
54	247	2.6	3.11	59.3	0.90	..	2.40
55	243	15.0	3.06	16.0	1.00	1.25	2.30
56	243	10.9	3.06	34.8	0.96	0.62	0.64
77	250	7.4	3.01	45.8	3.46	1.50	1.80
79	250	10.4	3.01	17.5	1.36	0.94	2.15
80^{D}	250	22.2	3.00	7.5	1.14	0.88	2.05
81^{D}	250	12.3	3.00	17.7	1.56	0.78	1.87
82	225	9.2	3.01	7.0	..	0.68	3.81
83^{D}	225	13.1	3.00	13.1	..	0.65	3.52
84	225	18.8	3.01	55.0	5.90	5.00	2.36
85^{D}	250	25.0	2.98	5.2	0.80	0.80	2.00

[a] D indicates methanol decomposition run. [b] Same units as in Table III.

Synthesis of Formaldehyde.—These runs were all made with the copper–zinc catalysts (Nos. 1, 11 and 12) at a pressure of 3 atmospheres absolute. The results are summarized in Table IV.

Since the effect of temperature on this equilibrium constant is small, the values for the first ten runs and that for run 85 have been averaged to give a value of $Kp = 1.72 \times 10^{-5}$ at 247°. For 225° the value of run No. 84 has been chosen as being the most reliable since the amount of formaldehyde produced was much greater than in any of the other runs. The fact that decomposition runs give constants of the same order of magnitude as those for synthesis is good evidence that the values cannot be far from equilibrium ones.

Discussion of Results

The following conclusions have been drawn from a study of all the runs on hydrogenation of formaldehyde.

1. Formaldehyde is readily and practically completely hydrogenated at temperatures from 120 to 200° over all of the catalysts except the osmium, platinum, and pure zinc catalysts which were quite inactive.

2. Nickel catalysts promote the decomposition of formaldehyde into carbon monoxide and hydrogen more than the copper catalysts. With the nickel catalysts, carbon monoxide was one of the major products even at as low a temperature as 120°, whereas with the copper catalysts, this was not the case until the temperature exceeded 150°, or usually higher.

3. In some of the runs, particularly with copper catalysts, relatively large amounts of methyl formate were produced. In one case nearly 80% of the carbon appeared in this form in the products.

4. The composition of the products from a given type of catalyst appears to be greatly influenced by slight variations in its structure caused either by variations in the method of preparation or changes that occur as the catalyst is used. Thus a given filling of catalyst No. 4 was used in three consecutive runs under as nearly identical conditions as could be maintained. In the first run, only 4% of the carbon in the products was in the form of methyl formate and 90% as methanol, whereas in the third run of the series, 78% appeared as methyl formate and 20% as methanol.

In order to deal with the equilibria over a range of temperatures, it is assumed that the variation of Kp with temperature may be represented by the equation

$$\log_{10} Kp = (-\Delta H/4.577) + C$$

Using the best available thermal data and evaluating C from the equilibrium constants given above, there are obtained the equations

$$\log_{10} Kp_1 = (374/T) - 5.431 \text{ (formaldehyde synthesis)} \quad (1)$$

$$\log_{10} Kp_2 = (4600/T) - 6.470 \text{ (hydrogenation of formaldehyde)} \quad (2)$$

A further proof that the measured equilibrium constants are of the correct order of magnitude may be had by calculating Kp_1 and Kp_2 for 250° by the above equations and comparing their product with the published values for the methanol equilibrium. $Kp_1 \times Kp_2$ at 250° $= 4 \times 10^{-3}$ and the values for the constant of the methanol synthesis equilibrium vary over the range from 1×10^{-3} to 5×10^{-3}.

To show what the possibilities are for the synthesis of formaldehyde from carbon monoxide and hydrogen and for the production of formaldehyde by dehydrogenation of methanol, results calculated from equations (1) and (2) are presented in Table V.

TABLE V

CALCULATED CONVERSIONS TO FORMALDEHYDE

Temp., °C.	Press., atm.	Kp_1	Kp_2	Percentage conversion to formaldehyde	
200	1	2.30×10^{-5}	1800	2.4	(Methanol dehydrogenation)
200	300	2.30×10^{-5}	1800	0.35	(Formaldehyde synthesis)
250	1	1.92×10^{-5}	210	6.9	(Methanol dehydrogenation)
350	1	1.48×10^{-5}	8.3	32.8	(Methanol dehydrogenation)
450	1	1.22×10^{-5}	0.8	74.5	(Methanol dehydrogenation)

The result for formaldehyde synthesis is based on the assumption that $CO + H_2 = HCOH$ is the only reaction taking place. As a matter of fact it has already been shown that formaldehyde is very easily hydrogenated and one can safely say that any catalyst that will promote the hydrogenation of carbon monoxide will certainly promote the further hydrogenation to methanol. The maximum possible yield of formaldehyde assuming that equilibrium is reached with respect to both reactions is readily calculated and is considerably less than the yield from the first step alone. For the specific case chosen, the conversion would be extremely small because of the high conversion to methanol that is possible. At 350° and 300 atm. about 0.10% would be the conversion to formaldehyde. We may, therefore, conclude that the direct synthesis of formaldehyde from carbon monoxide and hydrogen is not feasible at any reasonable temperature or pressure. Our results also show that none of the previous investigations of formaldehyde synthesis at atmospheric pressure would have yielded enough formaldehyde to give a positive test, confirming the conclusions of Marshall and Stedman.

It is also evident that methanol cannot be appreciably dehydrogenated to formaldehyde at temperatures of 200° and below, and to secure good yields temperatures of over 400° are necessary.

Summary

The position of equilibrium for the reactions $H_2 + CO \rightleftharpoons HCOH$ (1) and $H_2 + HCOH \rightleftharpoons CH_3OH$ (2), has been investigated at temperatures from 200–250° and at 1 to 3 atmospheres pressure. The best values for Kp are 1.72×10^{-5} at 247° for reaction (1) and 2090 at 197° for reaction (2). The following equations for the variation of Kp with temperature are

suggested: $\log_{10} Kp_1 = (374/T) - 5.431$ and $\log_{10} Kp_2 = (4600/T) - 6.470$. The significance of these results in the practical synthesis of formaldehyde is discussed.

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Thermodynamic Properties of Trifluorotrichloroethane and Difluorotetrachloroethane

BY FRANK HOVORKA AND FRANCIS E. GEIGER

In the study of the fluorination of hexachloroethane at high temperatures and pressures, Booth, Mong and Burchfield[1] obtained, among others, two liquid compounds, $C_2F_2Cl_4$ and $C_2F_3Cl_3$. A few of the more common physical constants were determined by them, but these only at one temperature. In view of the possible industrial importance of these liquids, it was considered quite desirable to determine accurately their physical constants over a wide range of temperature.

Purification of Materials.—The materials were furnished through the kindness of Dr. Booth of this Laboratory. The $C_2F_2Cl_4$ was refluxed over barium oxide to remove any water which might be present. Then it was fractionally distilled, using a special high fractionating column until a boiling point constant to 0.05° was obtained. Crystallization of this liquid did not affect the boiling point of the liquid. The $C_2F_3Cl_3$ on account of its low boiling point was distilled directly from barium oxide and condensed with carbon dioxide snow to avoid any excessive loss by evaporation. It was then fractionally distilled until a boiling point constant to 0.04° was obtained.

Apparatus and Procedure.—The various physical constants were determined by practically the same method as that described by Hovorka, Lankelma and Naujoks.[2]

Discussion of Results.—In the case of each liquid the boiling point was obtained by extrapolation of the vapor pressure–temperature curve. The heat of vaporization was calculated from the slope of a line obtained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Sugden's parachor and the critical temperature were obtained by the usual methods. All of these are summarized in Table I.

The freezing point of $C_2F_2Cl_4$ was found to be 28.1°. Its Eötvös constant was 2.34. All the other properties as shown in the Table exhibited the usual variation of a normal liquid.

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(1) Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).

(2) Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).