Methanol from Hydrogen and Carbon Monoxide[1]

Ralph L. Brown and A. E. Galloway

PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.

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The production of methanol from carbon monoxide and hydrogen under pressure has been studied comparatively with zinc oxide, basic zinc chromate, and normal zinc chromate as catalysts. The last two catalysts are more active than the zinc oxide, and at higher pressures and temperatures the normal chromate proved to be the more active of the three. It is a hardy catalyst. At 400° C. and 180 atmospheres, and in a theoretical mixture of hydrogen and carbon monoxide, an experimental conversion of the latter to methanol of about 20 per cent has been attained.

AS ONE phase of its study of the utilization of coal and with the ultimate need of synthetic motor fuels in mind, the United States Bureau of Mines has sought to provide itself in a general way with first-hand information on reactions and processes bearing on the production of liquid fuels from coal. As a first step in the work dealing with catalysts and pressure processes, a number of experiments on the synthesis of methanol from hydrogen and carbon monoxide have been made. With full cognizance of the present overproduction of petroleum and of the fact that the mass attack by large industrial research units has already led to quantity production of methanol in America,[2] the results of these first experiments are reported in view of the general interest in the subject. They are to be considered as results obtained for the particular preparations of catalysts used and under the specific conditions employed. The yields presented are comparable and relative, but are not necessarily ultimate values.

Brief Review of Results in Europe

Although there is much published discussion on the synthesis of methanol, that which presents actual experimental results is limited. In co-appearing papers in 1925, Patart[3] and Audibert[4] published results of their experimental studies. Patart stated that their choice of catalyst was based on the known principles of chemical thermodynamics, on the accepted conceptions of the role of a catalyst, and on considerations of equilibrium—that is to say, that a catalyst will function on either side of the equilibrium state and that catalysts which accelerate the splitting of methanol into carbon monoxide and hydrogen will likewise accelerate the formation of methanol from carbon monoxide and hydrogen. He also pointed out that Jahn[5] had decomposed methanol to give a gas containing 30 per cent of carbon monoxide, the remainder being hydrogen containing a trace of methane, by passing it over a heated mixture of zinc and zinc oxide, and that Sabatier[6] had done likewise with copper at 350° C. From the work of Jahn, Sabatier, Senderens, Mailhe, Ipatief, and others it was evident that copper, nickel, cobalt, platinum, palladium, zinc, etc., as well as many oxides of zinc, manganese, aluminum, cobalt, iron, vanadium, tin, thallium, tungsten, etc., split off one H_2 at moderate temperatures and broke up the resultant formaldehyde at higher temperatures into hydrogen and carbon monoxide. Patart reported the production of methanol, using pure zinc oxide as catalyst and employing temperatures of 400° to 420° C. and pressures of 150 to 250 atmospheres. In these experiments yields were not given and the crude product contained 80 per cent of methanol by volume, the remainder being apparently largely water. In his paper before the International Conference on Bituminous Coal in November, 1926, Patart stated that zinc oxide promoted with chromic oxide was the most satisfactory catalyst. In patent disclosures Patart[7] covers zinc oxide (>2 mols) plus metallic oxides of acid character and specifically named basic chromates, vanadates, tungstate, and manganese of zinc. A molecular mixture of 3 parts of zinc oxide to 1 part chromic oxide was favored for practical use.

Audibert, employing as catalysts an unnamed suboxide of uranium obtained by reduction of uranium oxide with hydrogen and a similarly treated chromic oxide at 275° to 300° C. and a pressure of 200 atmospheres, obtained methanol 99.5 per cent pure. The conversion of carbon monoxide to methanol per pass was estimated at 8 to 10 per cent (5000 space velocity).

In 1925 Patart[8] stated that up to that time their maximum conversion of carbon monoxide to methanol per pass with a space velocity of 10,000 was about 10 per cent, or 0.5 liter of methanol per hour per liter of catalyst.

The industrial production of synthetic methanol abroad has been known for some time and in May, 1927, an industrial production of 4500 gallons of methanol daily was announced by one American company.[2] In this instance, carbon dioxide and hydrogen, hitherto waste gases from the production of butanol and acetone from corn, were utilized. The catalysts employed were not stated, though numerous combinations of metal oxides have been disclosed by patents granted.[9] Conversions have not been made public.

The decomposition of methanol under heat alone and in the presence of various catalysts has been reported by Nef, 1901; Ipatief, 1906; Sabatier, 1904; and Tropsch and Schellenberg, of which a review was prepared in 1925 by Schellenberg.[10] An extended series of tests on decomposition by oxides has recently been made by Smith and Hawk.[11]

Apparatus

The apparatus shown in Figure 1 was one set up for general use. The unreacted gases could be recirculated in it. The reaction tube, 9, and the receiver, 13, were constructed of chrome-vanadium steel[12] lined with copper. The gas, in being introduced into the system, passed through chamber 1 containing reduced copper oxide heated to burn out traces of oxygen, and through calcium chloride and soda lime in chambers 2, 3, and 4. Any iron carbonyl in the gas was probably removed at the same time.[13] From the compressor, 5, and compressor tank, 6, the gas passed into the system through a tube which extended through a preheater, into the reaction chamber, 9, heated by an electric furnace and containing the catalyst, 11, and then through a coil, 12, cooled by ice and water to 1° or 2° C. and into the receiver, 13, cooled to several degrees below zero. The uncombined gases returned to the top of the reaction chamber through a circulating pump, 14, and a small condenser, 15, cooled to a temperature lower

[1] Published 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 73rd Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927. Received July 5, 1928. Since the presentation of this paper, the results of work by Audibert and Raineau in France, Lewis and Frolich in America, and Morgan, Taylor, and Hedley in England have appeared.

[2] Woodruff, IND. ENG. CHEM., **19**, 1147 (1927); Editorial, *Ibid.*, **19**, 547 (1927); *Ibid.*, News Edition, **5**, 4 (April 10, 1927).

[3] *Chimie et industrie*, **13**, 179 (1925).

[4] *Ibid.*, **13**, 186 (1925).

[5] *Ber.*, **12**, 983 (1880).

[6] Sabatier edition, 1913, p. 190, *Ann. chim. phys.*, **1905**, p. 418.

[7] British Patent 252,361 (May 25, 1925).

[8] *Bull. soc. encour. ind. nat.*, **13**, 141 (1925).

[9] Woodruff and Bloomfield, U. S. Patents 1,608,603; 1,608,643; 1,609,543; 1,625,924-5-6-7-8-9.

[10] *Abhandl. Kenntnis Kohle*, **7**, 9, 13 (1925).

[11] *J. Phys. Chem.*, **32**, 415 (1928).

[12] French, Bur. Standards, *Tech. Paper* **205** (1921–22).

[13] Fieldner and Jones, *Am. Gas Assoc. Monthly*, **6**, 439 (1924).

than the receiver previously mentioned. The tubing in the circuit was of copper and the pump was constructed of bronze. The temperature of the gas as it entered the reaction chamber was recorded by a thermocouple introduced into a copper well, 16, and the temperature of the catalyst mass was recorded from a thermocouple introduced into the catalyst by a well terminating at a point, 17, about the middle of the catalyst column. Temperatures were recorded by a potentiometer, 18.

Gas Used

The gas used in these experiments has consisted of essentially 2 parts of hydrogen and 1 part carbon monoxide. The carbon monoxide was prepared from formic and phosphoric acids, washed with water and alkali, and mixed with 2 volumes of commercial hydrogen as obtained in the usual steel cylinders. The gas contained an average of 1 per cent of methane or less, smaller quantities of carbon dioxide, and 3 to 5 per cent of nitrogen. These inerts averaged about 5 per cent (extreme limits 2.5 to 7.5 per cent). In the experiments reported, no purification further than that mentioned in the preceding paragraph was made. No trace of iron has been detected by chemical means in the catalysts used.

Catalysts

The catalysts were preparations of zinc oxide, basic zinc chromate, and normal zinc chromate which had been reduced. They were prepared in the following manner, without further purification of reagent or catalysts than is stated:

ZINC OXIDE—Basic zinc carbonate was precipitated from hot solutions of zinc nitrate and sodium carbonate. It was washed free from nitrates. The moist precipitate was pressed into threads of 2.4 mm. diameter, air-dried, and then slowly heated up to 300° C. under reduced pressure. The zinc oxide resulting from its decomposition was used directly.

BASIC ZINC CHROMATE—Zinc nitrate solution (496 grams $Zn(NO_3)_2$ in 2.4 liters H_2O) was added slowly to a dilute solution of sodium chromate (896 grams $Na_2CrO_4.10H_2O$). The precipitate was washed free from nitrates and pressed into threads. It was first air-dried, then dried at 80° C., and finally reduced in hydrogen at 300° C.

NORMAL ZINC CHROMATE—Following Gröger,[14] zinc oxide was ground with a little chromic acid solution to yield a paste. This was added to the remainder of the chromic acid solution and mechanically agitated 12 to 15 hours and the zinc chromate separated by filtration. The moist precipitate was pressed out, dried at 80° C., and reduced at 300° C.

Experimental Results

Thermodynamic calculations from existing data by Kelley[15] and by Christiansen[16] have given certain rough but widely divergent indications of the order of magnitude of the theoretical yields at 1 atmosphere, as they vary with temperature. From certain formulations of the Third Law, approximations of the yields obtainable under pressure can be made from existing heat data and are introduced later in this paper. In addition to yields, our experimental interest has been confined largely to the third fundamental factor—that of time. This means the rate of conversion of carbon monoxide to methanol and depends, in addition to temperature and pressure, broadly on the qualities of the catalyst. In its more general aspects, quality consists of high initial activity and continued activity or long life. (There are, of course, other factors, such as "ease of poisoning," absence of side reactions under conditions of industrial usage, etc.; their importance is somewhat specific with their particular industrial utilization.) It is also common knowledge that activity or, more strictly, efficiency in the prepared catalyst depends, in addition to its chemical composition and inherent physical properties, upon temperature, time of contact with the reactant gases, and the pressure of the latter.[17]

The introductory experiments into pressure syntheses and on the time factor were designed to give pressure-time curves for three known catalysts—zinc oxide, normal zinc chromate, and basic zinc chromate. The conditions were these: closed circulating system; catalysts, 250 cc.; system capacity (net), 2000 cc.; initial gas pressure, 280 atmospheres on the average, final, 100 atmospheres; temperatures, 300°, 350°, and 400° C.; make-up gas, none; rate of circulation, 12.5 passes per hour. The resultant curves are shown in Figures 2, 3, and 4, and the corresponding rate of pressure-drop curves appear in Figures 5, 6, and 7. These curves are approximate,

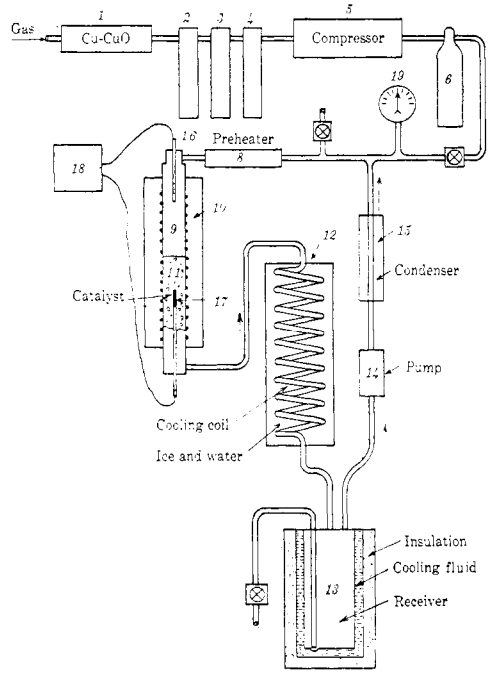

Figure 1—Diagram of Apparatus Used in Methanol Synthesis Experiments

because P is the apparent pressure. No account was taken of the effects of (1) reduction of physical volume of the system due to the methanol formed; (2) reduction of pressure due to the solubility of the reactant gases; (3) possible leaks (none existed at room temperature—at reacting temperatures they cannot be determined); (4) increase in inerts; (5) limited accuracy in gage readings; and (6) small irregularities in the temperature control of the system. (These factors are minor as regards our purpose and are somewhat self-compensating as will be evident later—Table II, column 7.) In Figures 5, 6, and 7, dP/dt (as atmospheres per minute) is plotted against pressure. In the case of zinc oxide (Figure 5) the rate of methanol formation at 310° C. was low and practically constant; it was roughly insensitive to change in pressure but responsive to temperature increase. In the curve for 355° C., the activity has become such as to show dP/dt

[14] *Z. anorg. Chem.*, **70**, 135 (1911).
[15] IND. ENG. CHEM., **18**, 78 (1926).
[16] *J. Chem. Soc.* (*London*), Pt. I, 413 (1926).
[17] Larson has found in case of ammonia synthesis that the efficiency of the catalyst falls off with increased pressures and space velocity, and that this ΔE increases with decrease of temperature and impurities in the gas. See Larson, Newton, Hawkins, Brooks, and Tour, *Chem. Met. Eng.*, **26**, 493, 555, 588, 647 (1922).

sensitive to pressure change. The greater activity at 400° C. under the conditions employed is evident.

In the case of the normal zinc chromate the curves of Figure 6 show that the rate of methanol formation per volume of catalyst was materially faster at all three temperatures. (The mass relationships of these catalysts are given in Table II.) For the basic chromate the rate per volume of catalyst was also materially greater than that of zinc oxide at corresponding temperatures and less than the normal salt at the upper range of temperature. The two chromates

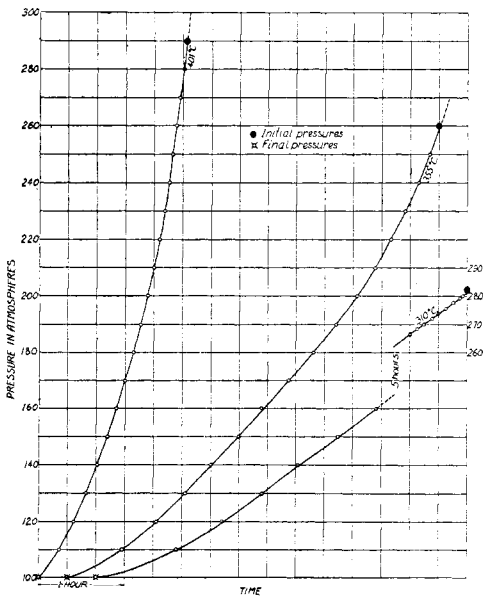

Figure 2—Pressure-Time Curve. Catalyst No. 5, ZnO

appear to have at least reached, under the conditions of these experiments, their maximum activity by about 400° C.; also, the relative positions of the sets of curves suggest that the "promoter" effect of the chromic oxide may be greater in the normal chromate around 350° C. and for the basic salt nearer 300° C., although the sensitiveness to temperature may also be involved. Our program is intended to give further information on this point. The maxima (inflections) in the curves at 300° C. in Figures 6 and 7 are due to a combination of effects arising at the start of those runs. These may include a relative colder top portion of the catalyst mass due to the larger heat capacity per unit volume of the compressed gases, the higher space velocities, and the lower activity of these catalysts at 300°. It is well known that a catalyst functioning towards the lower limit of its activity range loses in efficiency rapidly with increase of either pressure or space velocity.

The question of temperature control is a complicated one. With a strongly exothermic reaction like that of methanol, and with a sizable amount of catalyst, local overheating within the catalyst is encountered or else the gas introduced at lower than the desired reaction temperatures gives rise in some instances to cold top layers of catalyst. This may be ameliorated or obviated with various ingenious heat-conducting devices, interchangers, dilution of reactant gases with reaction products, one reactant or inerts, or by other artifices, but each catalyst with a different activity employed under any standard set of conditions means that a different amount of heat largely internal to the catalyst mass has to be considered. As our ultimate aim was an exploratory one with respect to catalysts, and hence partly qualitative, and also because our interest centered in the nature of the products, we chose to introduce the gas into the reaction chamber at a temperature near that desired and still maintain the one desired within the catalyst mass.

REACTION PRODUCTS—The liquid products from the runs for which the curves are given were examined as to weight, specific gravity, distillation characteristics, and percentage of methanol. The percentage of methanol was checked against an estimated amount calculated from the pressure drop and the volume of the system with the proper allowance for temperature and other corrections. Table I gives the results.

Table I—Variation of Approximate Yields of Methanol with Temperature

CATALYST	TEMP.	METHANOL CALCD. FROM PRESSURE DROP	METHANOL FOUND			
			Crude	Pure	Purity	% of calcd. methanol
(1)	(2)	(3)	(4)	(5)	(6)	(7)
	° C.	*Grams*	*Grams*	*Grams*	%	%
Zinc oxide	400	160	128.5	122.1	95	76+
	355	...	...	...	..	..
	310	115.7	84	80	95	70
Normal zinc chromate	400	150	125	120	96	80
	380	148.4	128	125.4	98	85
	353	143.0	137.3	133.9	97.5	94
	305	145.4	125.5	124.3	99−	86
Basic zinc chromate	406	154.1	126.5	116.5	92.4	76
	395	128.8	109.2	99.7	91.3	77
	350 (*a*)	124.4	123.5	114.9	93.0	92
	(*b*)	136.6	124.7	120.9	96.9	89
	305	127.9	119	115.7	97.2	90

The third and last columns are but approximations, since the values are based on the frank assumption that the contraction in volume is equivalent to that of methanol, whereas we know that gaseous by-products, water, and a trace of oil are involved. The table does serve, however, to give the general picture we desired. Thermodynamic considerations, of course, favor the lowest working temperatures, and the values of the last column show that at temperatures around 350° C. in these experiments the least amount of side reactions occurred, although a time factor is probably involved

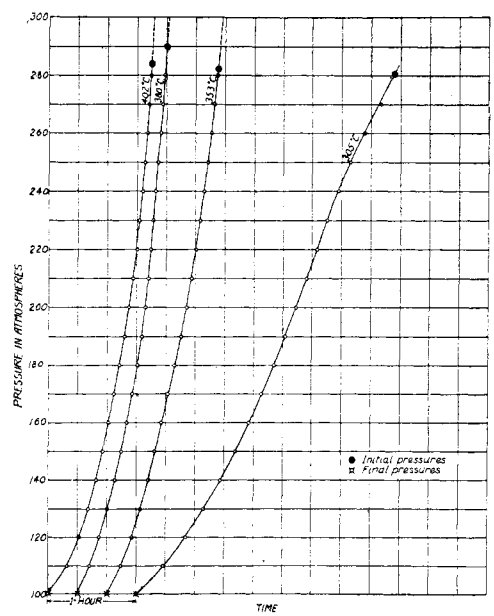

Figure 3—Pressure-Time Curve. Catalyst No. 3, Zinc Chromate

at the low temperatures—whether the side reactions arise from the composition of the catalysts or of the metals of the system. (For a long preliminary test of the pumping mechanism a hastily prepared zinc oxide of low methanol activity was introduced. It produced at 400° C. as much methane as it did methanol.)

The distillation characteristics of the crude methanols of the second group in Table I are shown in Figure 8. The relative variations with temperature are typical and the principal impurity is water. A few tenths of 1 per cent of an oil are normally present.

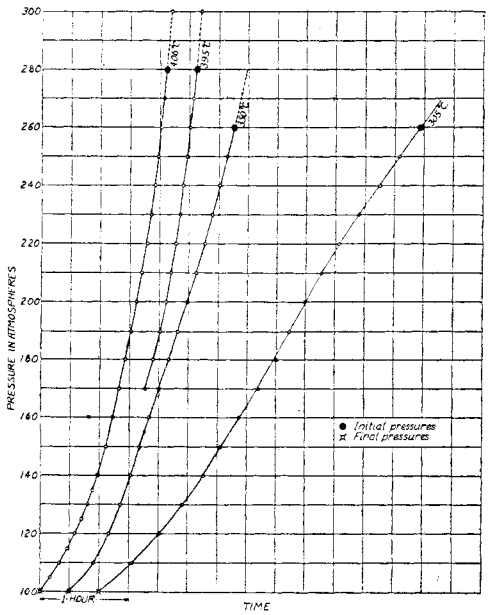

Figure 4—Pressure-Time Curve. Catalyst No. 4, Basic Zinc Chromate

The principal gaseous by-product was methane; at times there were traces of carbon dioxide, and, with the chromate catalysts, there was a trace of ethane.

Constant-Pressure Experiments

With the general picture just presented a limited program of comparative 1-hour tests at constant pressure (200 atmospheres) was outlined. These catalysts were to be tested at several temperatures. At this time the tests at 400° C. have been completed. Space velocities of 3000, 7500, and 16,200 have been used. The methanol produced in 1 hour under the prescribed conditions was weighed and its purity determined. At this stage of the study, the degree of drying of the gas mixture was increased and the crude methanol produced in these tests at 400° C. regularly contained 97 per cent of methanol, within 0.2 or 0.3. The gas in the system at the outset of each run contained 5 per cent total inerts and the run was continued from 1 hour up to 2 hours, depending on the activity of the individual catalyst. The resultant gas in all cases contained just about 15 per cent of total inerts. The average actual effective pressure of $CO:2H_2$ was 90 per cent of 200 or 180 atmospheres. Table II gives the results.

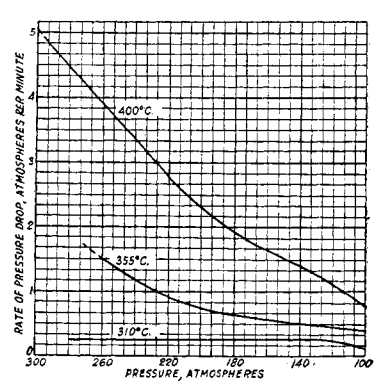

Figure 5—Approximate Rates of Pressure Drop with Zinc Oxide as Catalyst

Columns 5 and 7 give the methanol produced per hour by equal volumes of the indicated catalysts under like conditions; columns 6 and 8 give the per cent of carbon monoxide converted into methanol per pass over these catalysts under those conditions. The figures in parentheses (column 7) represent the methanol estimated from the rate of pressure drop as read graphically from curves in Figures 2, 3, and 4. The check in the case of the mixed catalysts is good. In the case of zinc oxide the larger difference is probably due to a greater amount of side reactions; certainly the methane produced in this run was relatively high. From Table II and Figures 5, 6, and 7, the further suggestive relations are available. (Table III)

Table II—Comparative Hourly Production of Methanol at 400° and 180 Atmospheres

Crude methanol (97% CH_3OH) produced

Catalyst (before reduction)	Volume	Weight Reduced	ZnO Content by Analysis	S. V. 7500 Production	S. V. 7500 Conversion CO-CH_3OH per pass	S. V. 16,200 Production	S. V. 16,200 Conversion CO-CH_3OH per pass
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Cc.	*Grams*	*Grams*	*G./hr.*	*%*	*G./hr.*	*%*
Zinc oxide	250	60	60	68	8.2	87 (94)	4.5
Basic zinc chromate[a]	250	165	112.5	..	..	137.5 (139)	7.4
Normal zinc chromate[a]	250	242	105.5	130	16.8	184 (186)	9.6
				S. V. 3000			
				71	19.5		

[a] These catalysts as used after reduction are considered to be, respectively, $2ZnO.{}^1/_2Cr_2O_3$ and $ZnO.{}^1/_2Cr_2O_3$. For convenience they have been designated as above throughout this paper.

Table III—Variation of Methanol Production with Catalyst Volume, Mass, and Zinc Oxide Content

Catalyst	Methanol Produced: Per unit volume catalyst	Per gram catalyst	Per gram ZnO in catalyst	Pressure Drop: 400° C.	350° C.	300° C.
(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Grams per hour			*Atm. per minute*		
Zinc oxide	87	1.45	1.45	2.25	0.75	0.25
Basic zinc chromate	137.5	0.83	1.22	3.0	1.75	1.9
Normal zinc chromate	184	0.76	1.75	4.0	2.90	1.5

From column 3 it is evident that alone chromic oxide must possess a low activity for methanol production compared to zinc oxide, although its known "promoter" influence is manifest in columns 2 and 4. That the value of 1.22 (column 4) for the second catalyst is less than the 1.45 for zinc oxide is thought to be due to the fact that the maximal conversion (at its optimum temperature for the 16,200 space velocity) is further below 400° C. than is the case for the other two catalysts; this, we think, is also indicated by the figures of the three remaining columns. Our program will definitely clear this point.

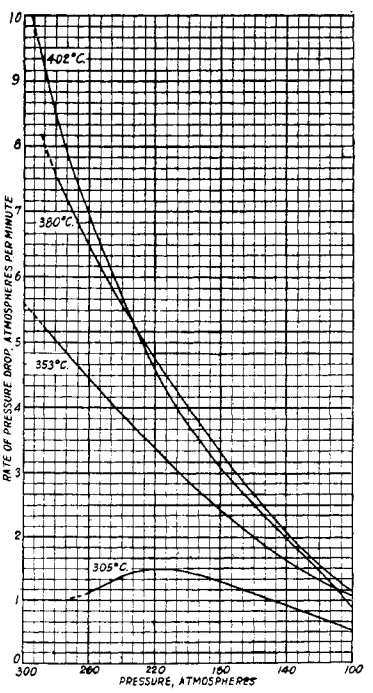

Figure 6—Approximate Rates of Pressure Drop with Reduced Normal Zinc Chromate as Catalyst

Life and Preparation of Catalysts

During the course of the work certain indications on the life of these catalysts have become definite. The activity of the zinc oxide as prepared and used in these experiments has been noted to decrease rapidly with usage. (Table IV)

Table IV—Life of Zinc Oxide at 400° C.
All tests at 180 atm. and 400° C. pressure

Catalyst ZnO	Volume	Weight	Methanol Produced			
			S. V. 16,200		S. V. 7500	
			Production	Conversion per pass	Production	Conversion per pass
	Cc.	*Grams*	*Grams/hour*	*%*	*Grams/hour*	*%*
Freshly prepared	125	90	127	6.7	..	..
Used 1 hour	125	90	105	5.5	66.3	8.2
Freshly prepared	250	60	85	4.45	..	..
Used 5 hours	250	60	51	3.0	43	5.75

In tests on the heat of reaction and its influence on the control of the catalyst temperature at different temperatures and space velocities, one batch of normal zinc chromate was employed for period of 30 hours (17 hours at 300° C., 8 hours at 350° C., 3 hours at 400° C., 2 hours at 425° C.). The decrease in activity over this period was 15 per cent, which is much less than that noted in Table IV for zinc oxide.

In the preparation of catalysts, certain variations in activity cannot always be accounted for. However, it is in general true that the temperature of reduction must be controlled and it is desirable to hold the temperature as low as possible to obtain high activity in the catalyst; this makes it essential to control the heat evolved in the reduction. Observations on the relation of conditions of reduction to catalytic activity in the case of basic zinc chromate, for example, are given in Table V.

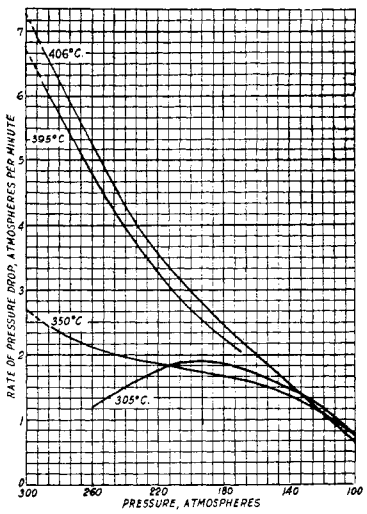

Figure 7—Approximate Rates of Pressure Drop with Basic Zinc Chromate as Catalyst

Table V—Relation of Method of Reduction to Activity of Catalyst
Catalyst—reduced basic zinc chromate
Conditions of test, 180 atmospheres, 400° C.

Catalyst	Volume	Weight	ZnO Content	Methanol Yield		Conditions of reduction
				S. V. 16,200	S. V. 7500	
	Cc.	*Grams*	*Grams*	*Grams per hour*		
I	250	165	112.5	129.3	..	At 40 atm. of $CO:H_2$, 1:2 mixture; temperature raised slowly from 25° to 370° C.
II	250	153	104	89.2	60.8	H_2, 1 atm.; reduction initiated at 300° C. but temperature uncontrolled, permitted to rise above 450° C.
III	250	170	115.5	106.4	94.5	Reduced at 275–325° C. at 1 atm. with a mixture of 5% H_2 and 95% CO

In the case of catalyst III whose temperature of reduction was carefully held down, the activity to methanol formation is clearly greater than that of catalyst II, which was reduced at higher temperatures. The activity of catalyst I is clearly the greatest. At this time it is not certain whether or not the apparent variations in conditions of reduction—that is, under pressure and in place—are the only ones responsible for the markedly higher activity of catalyst I.

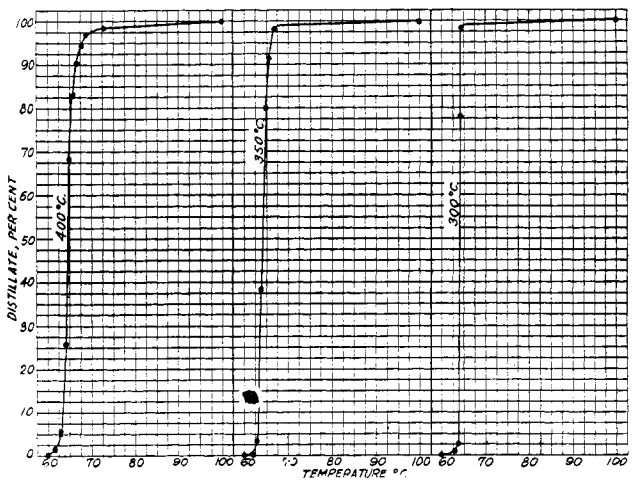

Figure 8—Methanol Distillation Curves, Catalysts, Zinc Chromate

Space-Time Yields

The agreement in the amount of methanol produced at 200 atmospheres (total pressure) during 1 hour (column 7, Table II) with that read from the pressure-temperature curve at 400° C. in Figure 3 has led to an estimation of space-time yields at that and higher pressures for the reduced normal zinc chromate. These are of the approximate magnitudes shown in Table VI.

Table VI—Approximate Space-Time Yields with Zinc Chromate at 400° C.

Pressure		Methanol per Liter Catalyst per Hour	Space Velocity
Total	Effective ($CO:2H_2$)		
Atm.	*Atm.*	*Kg.*	
200	180	0.73	16,200
270	245	1.4	22,000
300	270	2.15[a]	24,300

[a] This value has been frankly estimated from an extrapolation of the curve in Figure 3.

Equilibrium at 400° C.

When employing the reduced normal zinc chromate as catalyst at 400° C. and 180 atmospheres reactant pressure, a conversion of 9.6 per cent was obtained at a space velocity of 16,200, 16.8 per cent at 7500, and 19.5 per cent at 3000. When plotted, these show the conversion value to be approaching an apparent equilibrium value of the general order of 20 per cent. Bearing in mind that our values may be approximate and ignoring, for the present, side reactions and their possible complications, we have sought to compare our values with the expected theoretical conversions.

The approximate theoretical conversions for our working conditions of 400° C. and 180 atmospheres were first sought from the values of K_p calculated by Kelley[15] from existing thermodynamic data by means of free-energy equations. At 400° C. Kelley's value of

$$K_p = \frac{P_{MeOH}}{P_{CO} \times P_{H_2}^2}$$

equals 0.0033. Considering the reaction

$$CO + 2H_2 = CH_3OH$$

in a theoretical mixture we may set up these relations:

$$P_{MeOH} = 0.0033 \times [P_{H_2}]^2 \times P_{CO}$$
$$P_{H_2} = 2P_{CO}$$
$$P_{CO} + P_{H_2} + P_M = 180$$

From these its follows that, at equilibrium $P_{CO} = 20.74$, $P_{H_2} = 41.48$, and $P_{MeOH} = 117.78$ atmospheres, and the theoretical conversion would therefore equal 117.78/(117.78 + 20.74) or 85 per cent.

In view of the wide discrepancy between this 85 per cent and our experimental conversions, and because of the assumptions as to certain specific heat data used in Kelley's calculations, we have in a further comparison the approximation formula form of the Nernst heat theorem

$$\log K_p^1 = \frac{[P_{CO}] \times [P_{H_2}]^2}{P_{MeOH}} = -\frac{Q}{4.571T} + \Sigma\nu 1.75 \log T + \Sigma\nu C \quad (1)$$

In the calculation of Q the data employed for the heats of formation at 15° C. for carbon monoxide, carbon dioxide, and water were, respectively, 26.1, 94.27, and 68.40 calories, as found in Landolt-Börnstein Tabellen (5th ed.). The heat of combustion to methanol to carbon dioxide and water (l) at 15° C. as calculated by Smith[18] from the Richard and Davis data was taken as 179.900 calories. For the calculation of the chemical constant of methanol, $\frac{0.14\lambda}{T_{BP}}$ has the value $0.14 \times 8430/337.6 = 3.50$. Hence, $Q = 25{,}070$, and $\Sigma\nu C = 2 \times 1.6 + 3.5 - 3.50 = 3.20$, when the conventional values for hydrogen and carbon monoxide are taken. When these terms are inserted in equation (1), the following values of K_p^1 are obtained and from them their reciprocals K_p:

	300° C.	325° C.	350° C.	375° C.	400° C.	425° C.
$K_p^1[\times 10^3]$	1.93	5.61	15.10	37.86	89.13	189.34
$K_p[\times 10^{-5}]$	60.6	17.8	6.62	2.64	1.12	0.53

These values are much lower than the corresponding values of Kelley and will in turn be compared with the experimental value at 400°.

Experimental *K*'s

Based on the experimental conversion of 19.5 per cent of carbon monoxide to methanol in a mixture of $CO + 2H_2$, and on the assumption of perfect gas behavior for all three gases at 400° C., we have calculated the $K_p\left(\frac{P_M}{P_{CO} \times P_{H_2}^2}\right)$ obtained in our work to be 1.98×10^{-5}. Similarly, for the 17 per cent conversion a value of 1.6×10^{-5} is obtained.

However, it is well known that methanol departs widely from perfect gas behavior, and the magnitude of its departure is given by its fugacity at 400° C. This was calculated according to Lewis and Randall[19] by means of the van der Waal constants as given in the Landolt-Börnstein Tabellen. The results are shown graphically in Figure 9, in which the fugacity is seen to be about 55 atmospheres less than the pressure at 180 atmospheres. In this figure similar curves for carbon monoxide and hydrogen are also shown, both calculated in the same way. As is evident, carbon monoxide, like hydrogen, has a fugacity greater than the corresponding pressure. As we now have the approximate deviations of these gases at the average working pressure of 180 atmospheres in terms of their fugacities as calculated above, it is possible to introduce a correction for the failure of methanol to behave as a perfect gas; and as we also have the approximate fugacities for carbon monoxide and hydrogen, we have likewise employed in recalculating the approximate K's obtained experimentally by us at 400° C. In doing this we have employed the partial fugacities, obtained by multiplying the fugacities at 180 atmospheres by the respective mol fractions derived from our experimental conversions. The values employed for these terms for (*a*) 17 and (*b*) 19.5 per cent conversions, are given in Table VII.

Table VII—Fugacities at 400° C. and 180 Atmospheres

Gas	Fugacity	Mol Fraction		Partial Fugacities	
		(*a*)	(*b*)	(*a*)	(*b*)
	Atm.			*Atm.*	*Atm.*
CO	190.0	0.312	0.308	59.3	58.6
H_2	195.8	0.624	0.617	122.2	120.8
CH_3OH	123.8	0.064	0.075	7.9+	9.25

The recalculated K has been designated K_f and the values obtained for it from the highest experimental conversions at 400° C. are about 0.9×10^{-5} and 1.1×10^{-5}, respectively. These are in good agreement with the approximate value, 1.12×10^{-5}, given by the Nernst formula.

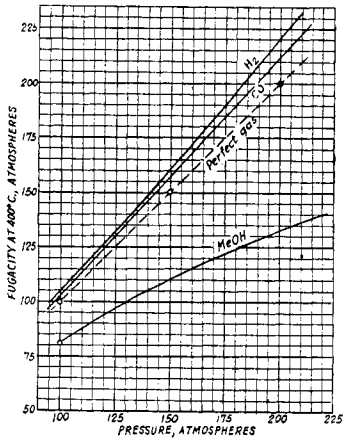

Figure 9—Fugacities for Carbon Monoxide, Hydrogen, and Methanol. Calculated from van der Waal's Constants (400° C.)

In the absence of established values for the water gas–methanol equilibrium upon which to base calculations of theoretical yields for various temperatures, we have sought on the basis of our established conversion of about 20 per cent at 400° C. to estimate approximate percentage conversions at other temperatures direct from the Nernst formula employed in an empirical manner. By taking $Q = 27{,}000$ as employed by Rideal and Taylor,[20] and the chemical constant for methanol as 3.1, the average value for unknown compounds suggested by Nernst, K_p at 400° C. calculates to be 1.9×10^{-5}, which agrees sufficiently well with the 1.98×10^{-5} calculated from our experimental conversion on the assumption of perfect gas behavior. Accepting the agree-

[20] "Catalysis in Theory and Practice," 2nd ed., p. 258.

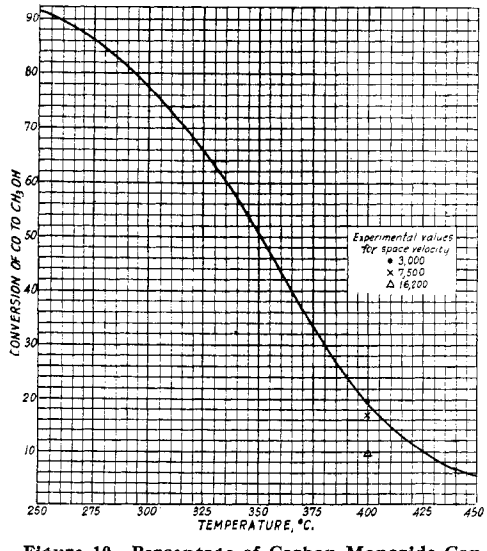

Figure 10—Percentage of Carbon Monoxide Converted to Methanol at 180 Atmospheres as Calculated by Nernst Approximation Formula

[18] IND. ENG. CHEM., **19**, 802 (1927).

[19] "Thermodynamics and the Free Energy of Chemical Substances," p. 196, McGraw-Hill Book Co., 1923.

ment at this one point as sufficient to permit the approximations desired, we have let Y equal the mol fraction of carbon monoxide converted to methanol and P equal the total pressure, then for the reaction $CO + 2H_2 \longrightarrow CH_3OH$

$$K_p^1 = \frac{[P_{CO}^1] \times [P_{H_2}^1]^2}{[P_{MeOH}]} = P\frac{1-Y}{3-2Y} \times \frac{4P^2(1-Y)^2}{(3-2Y)^2} \times \frac{1}{\frac{PY}{3-2Y}} = \frac{4P^2(1-Y)^3}{Y(3-2Y)^2}$$

$$\text{and } \log K_p^1 = \log \frac{(1-Y)^3}{Y(3-2Y)^2} + 2 \log P + \log 4.0$$

Substituting for $\log K_p^1$ in the approximation formula (1), we have

$$\log \frac{(1-Y)^3}{Y(3-2Y)^2} = -\frac{Q}{4.571T} + \Sigma\nu 1.75 \log T + \Sigma\nu C - 2 \log P - \log 4 \quad (2)$$

which reduces to

$$\log \frac{(1-Y)^3}{Y(3-2Y)^2} = -\frac{Q}{4.571T} + 3.5 \log T + 2.9979 - 2 \log P$$

The values obtained for Y in our calculations are graphically represented in Figure 10. Although possibly approximate, this curve gives a good estimate of possible yields under a reactant pressure of 180 atmospheres. Our experimental conversions at 400° C. have been indicated in Figure 10.

Acknowledgment

The writers are indebted to W. P. Yant, in charge of the gas laboratory, and his staff for many gas analyses, and to A. C. Fieldner, chief chemist of the Bureau of Mines, for his interest and patient support of this investigation.

Textures of Ice Creams as Influenced by Some Constituents[1]

Meta H. Given

HOME ECONOMICS DEPARTMENT, EVAPORATED MILK ASSOCIATION, CHICAGO, ILL.

Water in the ice-cream mix freezes into crystals. The fineness or coarseness of the texture of ice cream depends upon the size of the ice crystals. The size of the crystal depends upon the even distribution of numerous tiny air bubbles in the ice cream, which in turn depend upon the viscosity of the mix.

Mixes containing gelatin, eggs, and dry egg yolk show greater viscosities than the check. Although the variations in the viscosity readings are not great, the differences are much more apparent in handling the mixtures. Homogenization and aging increase viscosity. A single homogenized constituent like evaporated milk increases the viscosity and improves texture equal to that of 0.3 per cent gelatin, 2.5 per cent raw egg, or 0.3 per cent egg yolk.

ONE of the most agreeable qualities in ice cream is fine, velvety texture, free from lumps of fat and ice. Those familiar with the production of ice cream know that texture is dependent upon the constituents of the mix, the proportion and condition of those constituents, and the technic used in freezing. This paper has to do with the effect of some constituents on texture.

Influence of Constituents on Water Crystal Formation

Ice cream contains from 60 to 70 per cent water and from 30 to 40 per cent solids. Since the milk fat exists in microscopic globules in emulsion, the sugar in true solution, and the milk proteins principally in colloidal solution, ice cream is a complex mixture from both physical and chemical standpoints.

In the freezing process the water of the mix congeals into tiny crystals. The finest possible crystals are desired, so fine that they can be scarcely felt on the tongue. The tongue test is a reliable, practical, and delicate one for judging texture. The microscope, however, reveals crystals that cannot be felt on the tongue, and is therefore our most useful aid in making fine distinctions between ice creams.

It is well known that if water alone is frozen in an ice-cream freezer and beaten, an icy mush consisting of large crystals results; if the mass is not beaten, a solid lump of ice forms. In ice-cream mixtures the solids in true and colloidal solution interfere with the formation of large water crystals. The size of the solid particles in emulsion also has an influence on the texture.[2]

Microscopic examinations of fine-textured ice cream always show numerous tiny water crystals with small, well-distributed air cells. Grainy textured creams show large and irregular shaped crystals with large air cells less evenly distributed. The incorporation of a large amount of air in such a way that it is evenly distributed in tiny bubbles throughout the ice cream, therefore, is a condition of fine texture.

When viscous mixtures are beaten they are stretched out into thin, cohering films, which readily envelop air in very small sacks throughout the mass. This is why egg white permits so much air to be beaten into it. Air may be beaten into ice-cream mixtures also, provided the viscosity of the mixture is sufficient to retain the necessary amount of air. The value of these small and numerous air cells depends on the fact that the air acts as so much intervening solid substance between the water crystals, preventing the merging of many small crystals into a few large ones. It is a well-known physical principle that a tiny air bubble will withstand more pressure from the outside than a large one. This explains why fine-textured, firm-bodied ice creams remain smooth on standing, while light, fluffy ice creams containing large air bubbles settle and acquire a very coarse texture. The quality of the ice cream, then, is greatly affected by the quantity of the air incorporated, as well as by the size of the air cells. Experimental work of Ruehe[3] and of Mortensen[4] demonstrates this fact.

Manufacturers' Practices

Manufacturers have learned that viscosity may be greatly increased by the introduction of solids other than milk solids into the mixture. Some of the substances used are gelatin,[5] cornstarch, gum tragacanth, dried egg yolk, and whole egg.[6]

[1] Received April 7, 1928. Paper presented before the Biological Division of the Chicago Section of the American Chemical Society, February 24, 1928.

[2] Brainerd, Virginia Agr. Expt. Sta., *Tech. Bull.* **7**.

[3] *Ice Cream Trade J.*, **20**, 57 (1924).

[4] *Ibid.*, **20**, 74 (1924).

[5] Sommer, *Ibid.*, **23**, 47 (1927).

[6] *Ibid.*, **23**, 64 (1927).