

the entering carbon monoxide being converted to methanol. The catalysts low in cerium oxide possess marked resistance to heat, giving a maximum conversion of 82 per cent, but lose this property very rapidly for Ce-Cu ratios above 10:100.

Table V—Copper-Manganese Oxide Catalysts

Catalyst	Atoms Mn per Atom Cu	Load Density	Maximum Per Cent CO to Methanol			
			Untreated		Preheated	
			% Con- version	° C.	% Con- version	° C.
713	0.0900	0.90	21.8	387	17.0	385
725	0.0050	0.96	44.3	348	16.7	390
724	0.0125	1.03	49.3	345	14.2	395
723	0.0250	0.87	81.6	333	0.0	...
722	0.0500	0.93	48.7	348	18.0	377
721	0.1250	0.90	46.7	342	31.3	362
720	0.2500	0.84	56.7	345	39.3	360
719	0.3750	0.87	70.6	315	62.0	338
718	0.5000	0.97	76.0	265	56.4	315
615	1.0000	1.03	78.0	330	51.0	352

COPPER AND BERYLLIUM OXIDE—Besides increasing the initial activity, additions of beryllium have the advantage of yielding the most heat-resistant catalysts of this whole series, as is brought out by the curves in Figures 8 and 9, showing a maximum conversion of about 91 per cent for the heat-treated mixture of Be-Cu ratio 6:100.

Summary and Conclusions

From the results presented in this paper it is apparent that a number of substances which decompose methanol at elevated temperature and atmospheric pressure are capable of catalyz-

ing the synthesis of the alcohol by the reverse reaction using carbon monoxide and hydrogen at high pressure.

Reduced copper and zinc oxide are the most active of the methanol catalysts studied. Manganous oxide and chromium sesquioxide are of a considerably lower order, and the remaining oxides are too inactive to consider it worth while to employ them alone.

The method of preparing the catalysts is of utmost importance. This has been brought out particularly by the extensive studies of copper, showing that cuprous and cupric oxides give active catalysts with reduction by hydrogen, when prepared by precipitation of the nitrate or by thermal decomposition of the unstable copper salts of organic acids. It is essential that the reduction be carried out at low temperature. Copper catalysts prepared from the hydroxide precipitated from solutions of the sulfate and chloride are entirely inactive.

All of these single-component catalysts are very sensitive to heat, as has been brought out by the lowering in methanol conversion resulting from heat treatment somewhat above the temperature of operation.

In general, mixed catalysts are superior to single-component catalysts, as manifested both by the great increase in the rate of methanol production and by the greater resistance to heat.

In regard to the behavior of mixed catalysts, the material here presented does not permit of any definite conclusions. The data plotted for a large variety of such mixtures in Figures 8 and 9 are too erratic for a simple interpretation.

Comparative Study of Values Obtained in Synthesis of Methanol^{1,2}

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THE writers have found it interesting to make a comparative study of the values obtained in the work of Audibert and Raineau³ with their own and that recently published by Lewis and Frolich.⁴ In this they have limited themselves to one temperature, 400° C., for which their results have been published.⁵

Audibert and Raineau have employed the Nernst approximation formula in a form involving the total pressure under which the reaction is carried out. The development for the methanol reaction of this form of that equation is the following:

For the reaction

$$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH} + Q \text{ calories} \quad (1)$$
 we have after Nernst

$$\log K^1_p = \frac{-Q}{4.571 T} + \Sigma v 1.75 \log T + \Sigma v C \quad (2)$$

Now if x represents the mol fraction of carbon monoxide converted to methanol and P represents the total pressure in atmospheres, then

$$K^1_p = \frac{[P_{\text{CO}}][P_{\text{H}_2}]^2}{[P_{\text{MeOH}}]} = \frac{P(1-x)}{3-2x} \frac{4P^2(1-x)^2}{(3-2x)^2} \frac{1}{3-2x} = \frac{4P^2(1-x)^3}{x(3-2x)^2}$$

$$\text{also } \log K^1_p = \log \frac{(1-x)^3}{x(3-2x)^2} + 2 \log P + \log 4$$

$$\text{and (2) becomes } \log \frac{(1-x)^3}{x(3-2x)^2} = \frac{-Q}{4.571 T} + \Sigma v 1.75 \log T + \Sigma v C - 2 \log P - \log 4.0$$

For the methanol reaction (1) we have this approximation:

$$\log \frac{(1-x)^3}{x(3-2x)^2} = \frac{-Q}{4.571 T} + 3.5 \log T + 2.99794 - 2 \log P \quad (3)$$

$$\text{since } \Sigma v C - \log 4 = 3.5 + (2 \times 1.6) - 3.1 - 0.60206 = 2.99794$$

Per Cent Conversions

Without entering into the accuracy of this method of calculation and accepting it as a suitable or even empirical representation of the conversions approached experimentally by Audibert and Raineau, the writers have made comparisons of their per cent conversions at 400° C. with those of other recently published work. Of these, Audibert and Raineau employed a very active catalyst and a medium space velocity of 5000; Lewis and Frolich term their catalyst as one of medium activity, and for comparison we have selected from their published results the maximum experimental value⁶ for their conversion at 400° C., namely, 26 per cent at a space velocity of about 625; Brown and Galloway used an active

¹ Received July 7, 1928.

² Since this discussion was written, the report of Morgan, Taylor, and Hedley in *J. Soc. Chem. Ind.*, 47, 117T (1928), has appeared. Their preliminary results on the methanol equilibrium under pressure are in close agreement with the Nernst approximation values of Audibert and hence with the maximum experimental values of this discussion. They have also found normal zinc chromate to be a very active catalyst and in agreement with Brown and Galloway more active than the basic chromate at high temperatures.

³ Page 1105, this issue.

⁴ *IND. ENG. CHEM.*, 20, 285 (1928).

⁵ *Ibid.*, 20, 960 (1928).

⁶ See Figure 5 of reference 2.

Table I—Comparison of Experimental and Calculated Conversions Obtained by Three Sets of Investigators

EXPERIMENTER	ORIGINAL GAS MIXTURE	TEM-	TOTAL PERA- PRES- SURE	CONVERSION CO TO METHANOL		PARTIAL PRESSURES ATTAINED EXPERIMENTALLY, CALCD. FROM PER CENT CONVERSION			K_p $\frac{P_m}{P_{CO} \times P_{H_2}^2}$	FUGACITIES (a) CALCD. FROM VAN DER WAAL'S CONSTANTS AT PRESSURES AND TEMPERATURE INDICATED; (b) $f \times$ MOL FRACTION			K_f $\frac{f_m}{f_{CO} \times f_{H_2}^2}$
				Exptl.	Calcd. by Nernst approximation formula	CO	H ₂	MeOH		CO	H ₂	MeOH	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
		° C.	Atm.	%	%	Atm.	Atm.	Atm.		Atm.	Atm.	Atm.	
Audibert and Raineau													
(x) (S. V. 5000)	CO + 5H ₂	400	150	22.5	24 ^a	20.95	122.97	6.08	1.92×10^{-5}	(a) 156	159.8	109.9	1.19×10^{-5}
(y) calculated from (x)	CO + 2H ₂	400	150	14.66	14.6	47.29	94.58	8.12	1.92×10^{-5}	(b) 49.18	100.76	5.952	
Lewis and Frolich (S. V. 625)	CO + 2.7H ₂	400	204	26	27.0	47.47	139.85	16.68	1.80×10^{-5}	(a) 216.3	225.5	134.3	0.91×10^{-5}
										(b) 50.33	154.87	10.981	
Brown and Galloway (S. V. 7500)	CO + 2H ₂	400	180	16.8	19.0	56.17	112.33	11.51	1.62×10^{-5}	(a) 190	195.8	123.8	0.89×10^{-5}
(S. V. 3000)	CO + 2H ₂	400	180	19.5	19.0	55.52	111.04	13.44	1.98×10^{-5}	(b) 59.29	122.19	7.912	
										(b) 58.6	120.78	9.25	1.08×10^{-5}

^a Our calculations give 22.4.

catalyst and relatively higher space velocities of 7500 and 3000. The full comparison is shown in Table I, in which the first four columns set forth the sets of experimental conditions. Column 5 gives the experimental conversions and column 6 the ones calculated as stated above. In columns 7, 8, and 9 are given the calculated partial pressures of the carbon monoxide, hydrogen, and methanol, respectively, as attained experimentally. They have been calculated on the basis of the experimental conversions of column 5. From these, K_p (column 10) has been calculated, assuming no departure from the perfect gas laws. It is evident that these values are of the same order of magnitude and possess a relative position which might be well expected from the activities of the respective catalysts and the relative space velocities employed. Audibert and Raineau employed a very active catalyst and a medium space velocity; Lewis and Frolich, a catalyst of medium activity and a low space velocity; whereas Brown and Galloway employed an active catalyst and relatively the highest space velocity in their (a) experiment and an intermediate one in their (b) experiment.

Fugacities

In further comparison of these experimentally attained K 's, it has also seemed interesting to take into account the departure from perfect gas behavior of the three gases which take part in the reaction. Methanol is particularly an offender in this respect, the extent of which is very apparent from Figure 9 of Brown and Galloway's paper which represents graphically the approximate fugacities for carbon monoxide, hydrogen, and methanol as calculated according to Lewis and Randall⁷ from van der Waal's constants for 400° C. for the range of pressures in which we were interested. The fugacities (or effective pressures) at the exact pressures employed by the three sets of investigators are given in the (a) values of columns 11, 12, and 13 of Table I; the (b) values of these same columns are the partial fugacities, being the (a) values multiplied by the respective mol fractions as proposed by Lewis and Randall. These latter have been used in arriving at the new set of K 's which have been designated K_f and are given in column 14 of Table I. As was the case for K_p , the relative values of K_f are of approximately the same order and much lower than the values of K_p calculated from thermodynamical data by Kelly,⁸ whose values are probably much too high.

Space-Time Yields

The space-time yields from each of the three publications under discussion may be roughly approximated for the one temperature being considered. (A) From Audibert and Raineau's work the calculated yield per cubic meter is 53 grams; this $\times 22.5/24.0 \times 5000/1000 = 248$ grams per liter per hour, which represents their maximum value for a space velocity of 5000; (B) from Lewis and Frolich⁹ the 13 cc. at 200 liters per hour ($\times 0.8 \times 1000$ cc./40 cc.) is equivalent to 260 grams per liter per hour at a space velocity of 5000; (C) from Brown and Galloway the interpolated yield is about 104 grams at 5000 (to correspond to the other two cases) and this 104 grams $\times 1000/250 = 416$ grams per liter per hour.

These cannot be compared directly because three conditions still differ—namely, (1) the pressure, (2) the ratio of carbon monoxide to hydrogen, and (3) the density of the catalyst. The last we shall neglect and for the other two we can make certain approximations.

In order to reduce the three yields being compared to their equivalent values for a CO:2H₂ mixture, we have proceeded as follows: In case A, in which CO:H₂ = 1:5, a 24.0 per cent theoretical conversion is equivalent to 14.6 per cent in a CO:2H₂ mixture, and in the latter the CO per unit volume of gas passed is twice that of the former; hence

$$248 \times \frac{14.6}{24} \times 2 = 300 \text{ grams per liter per hour at 150 atmospheres.}$$

In case B the ratio CO:H₂ is 1:2.7 and hence similarly for a 1:2 mixture the yield would be 260 grams $\times 22.6/27 \times 2.7/2.0 = 295$ grams per liter per hour at 204 atmospheres. In case C with a ratio CO:H₂ = 1:2, the value is 416 grams per liter per hour at 180 atmospheres.

By means of the Nernst formulation we have for the three cases calculated equilibrium conversions in per cent at the above pressures and 400° C. of 14.6, 22.6, 19.0, which have the ratio 1.0, 1.55, 1.30. The space-time yields approximated above have the ratios, respectively, 300, 295, 416, or 1.0, 1.0, 1.4.

While quantitative deductions from these ratios can hardly be drawn with safety, because in the tests in the two cases other than our own, in which 250 cc. were used, the amount of catalyst employed was but a small fraction of the liter to which the values above are approximated, it does seem evident, however, from the above ratios that the reduced normal zinc chromate is an effective catalyst under the conditions obtaining in this comparison.

In the conversions obtained by the three sets of investi-

⁸ See Figure 4 of reference 4.

⁷ "Thermodynamics and the Free Energy of Chemical Substances," p. 225, McGraw-Hill Book Co., 1923; see also Gillespie, *J. Am. Chem. Soc.*, **47**, 305 (1925); **48**, 28 (1926).

⁸ Kelley, *IND. ENG. CHEM.*, **18**, 78 (1926).

gators no attempts have apparently been made to establish complete equilibrium. It is noteworthy, however, that there is such close agreement between the results from the inde-

pendent laboratories, notwithstanding the differences in types of catalysts, in the probable purity of the reactant gases, the types of apparatus used, and other working conditions.

The Second International Nitrogen Conference¹

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THE first international nitrogen conference, held at Biarritz, Spain, in 1926, having proved worth while, a second conference was called for 1928. This second conference, sponsored by the nitrogen syndicates of France, Italy, Norway, England, and Germany, was held on board the *S. S. Lutzow* sailing from Venice and cruising the Adriatic Sea from April 30 to May 8. Altogether fifteen countries were represented, including the United States and Canada. About one hundred and fifty people were in attendance.

A number of delegates having brought their wives and daughters along, the conference was, in part, a social affair including dinner parties and dances on board and excursions over the cities and out into the country at the ports of call, which included the Island of Corfu, Greece, and Cattaro, Ragusa, Spalato, Sebenico, and Brioni on the Yugoslavian Coast.

From time to time during the trip, the ship's bugler called the delegates to conference where consideration was given to various matters relating to the production and utilization of nitrogen fertilizers. The first address, given by Julius Bueb, of the Stickstoff Syndikat of Berlin, Germany, dealt with the problem of nitrogen economics.

Nitrogen Economics

In this address it was pointed out that world prices for nitrogen have been decreasing since the spring of 1923 while average prices for the products of the farm have been on the increase during this same period. In Germany, for example, assuming that 1 pound of nitrogen will produce 20 pounds of grain, as the experimental work with this element indicates, a dollar invested in nitrogen in 1923-24 and applied to the cereal crops produced a return above the cost of the fertilizer of \$1.82. In 1926-27 this return amounted to \$3.81. As a result there was a marked increase in consumption of nitrogen in Germany which, during the year 1926-27, reached a total of 400,000 metric tons of the element. The world total for that year was 1,339,000 metric tons. This is equivalent to nearly 6.5 million tons of sulfate of ammonia or over 9 million tons of nitrate of soda.

In satisfying this demand for nitrogen the air-nitrogen industry has enjoyed tremendous growth. Of the world total production of over 1,600,000 tons of nitrogen estimated for 1927-28, considerably less than half had its origin in Chile and in by-product coke ovens. The development of the air-nitrogen industry, therefore, not only resulted in reducing the cost of nitrogen to the farmer, but made it possible to meet the increased demand for this element resulting therefrom. As Doctor Bueb said, "the synthetic nitrogen industry saved the world from high prices and famine" following the World War.

A further important contribution has been the production of a considerable variety of nitrogen compounds such as are needed best to meet the requirements of the several crops when grown under the wide variety of soil and climatic conditions that obtain in the different parts of the world. In this connection particular mention was made of the reception given to nitrate of lime, which must be regarded as being at least equal in value to nitrate of soda and even superior for those soils that are deficient in lime.

¹ Presented at fertilizer conference held at Wooster, Ohio, July 2, 1928.

The synthetic nitrogen industry may also be credited with stimulating investigation of the possibilities of the commercial production of very concentrated fertilizer compounds. Particular mention was made of Nitrophoska, a complete fertilizer containing as high as 60 per cent of nitrogen, phosphoric acid, and potash combined. Five types of Nitrophoska, having different formulas and analyses, are being sold in Germany and are being used by farmers with good results.

In commenting on Doctor Bueb's paper, the writer called attention to several questions raised which appeared to him to be of considerable significance to the agriculture of the United States. The first was the fact that nitrate of lime, in contrast to nitrate of soda, would seem to be well suited to the needs of crops that are being grown on alkali soils as well as on those that are deficient in lime.

The production of highly concentrated complete fertilizers, of which Nitrophoska is an ideal type, merits all possible encouragement. The ultimate economy in freight and handling charges is apparent. But there are equally important reasons for increasing the concentration of fertilizers. With high concentration is associated high solubility and availability. Constituents having harmful or, at least, unnecessary effects are eliminated. The tendency on the part of the farmer toward a one-sided fertilizer program is avoided. The quantities of actual nutrients applied per acre are quite likely to be larger if concentrated fertilizers are used. The net effect of their use is a considerable increase in agricultural efficiency.

There is now a marked tendency in central United States toward a larger use of complete fertilizers carrying more nitrogen and potash. The using up of the store of virgin fertility in the soils of this country; the growing intensity of our agriculture; the lower cost of fertilizer nitrogen; and the tendency toward row applications of fertilizers for such crops as corn all operate to move the practice in that direction. In Ohio, for example, the consumption of nitrogen increased from 1729 tons in 1924 to 2893 tons in 1927. Likewise potash consumption increased from 7502 to 8963 tons, while the quantity of phosphoric acid used during the same period decreased from 51,983 tons to 41,181 tons.

In the adjustment that has been taking place between the country and the city in the United States during the last eight years, over three million people have been lost from the farm. Economic pressure has caused in part a reversion of poor cultivated land to pasture, waste, and forest, and in part a more efficient use of both land and labor. In the latter case the acre consumption of fertilizer is increased and more power machinery is used with each reduction in the cost of these commodities. Tractors and combines are substituted for horse and man labor. Other similar adjustments are being made.

There is still abundant opportunity for choice between increasing the acreage under cultivation and farming more intensively the land already under the plow. Cheaper nitrogen would seem to favor the latter, since it offers distinct possibilities as to increased yields of the cereal and other field crops and at the same time permits of more effective utilization of pasture land than has hitherto been possible. In fact, if abundant supplies of cheap nitrogen become available and the response to propaganda in