Rate of Methanol Synthesis

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Although there have appeared many papers[1-4] dealing with measurements on the methanol synthesis, only the paper by G. Natta and his coworkers[5] provides the experimental data sufficient for kinetic interpretation of the methanol synthesis. On the basis of their experimental results, they have proposed a rate equation of the methanol synthesis, which contains a few constants to be determined by laborious measurements at high pressure.

In the course of our study[6] on catalysts for the methanol synthesis, we desired to

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[1] W. K. Lewis and P. K. Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928).

[2] P. K. Frolich, M. R. Fenske et al., ibid., **20**, 1327 (1928).

[3] D. S. Cryder and P. K. Frolich, ibid., **21**, 867 (1929).

[4] M. R. Fenske and P. K. Frolich, ibid., **21**, 1052 (1929).

[5] G. Natta, P. Pino et al., *La Chimica e L'Industria*, **35**, 705 (1953).

[6] H. Uchida and Y. Ogino, This Bulletin, **29**, 587 (1956).

obtain the rate constant from a small number of measurements. In order to obtain a rate equation, which is more convenient for this purpose than that by G. Natta et al., necessary experimental data have been prepared by carrying out measurements on the methanol synthesis in wide ranges of the pressure and the ratio of hydrogen to carbon monoxide.

Experimental Procedure

The synthesis was conducted in a reactor containing 5 cc. of a catalyst of 2—3 mm. size. The gas for the synthesis was introduced into the reactor from a pressure storage; and the decrease in the pressure in the storage served as a measure of the volume of the gas fed. The exit from the reactor was freed from methanol through an ice-cooled condenser, and the volume was determined by means of a gas-meter at atmospheric pressure. By assuming the stoichiometric methanol yield of the gas consumed in the reactor, the methanol concentration in the exit gas just having left the reactor and the conversion into methanol were calculated[*1].

Some series of the synthesis were made under different total pressures ranging from 90 to 150 kg./cm^2 at several different temperatures between 300 and 360°C with gases of varying H_2/CO ratios. Moreover, in order to obtain the kinetic data, each series of the experiments at a definite pressure, H_2/CO ratio, and temperature, was made at different space velocities between 1×10^4 and 1×10^5.

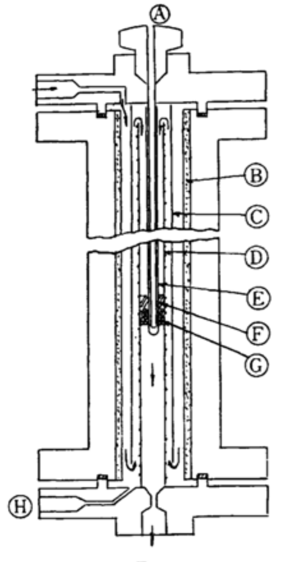
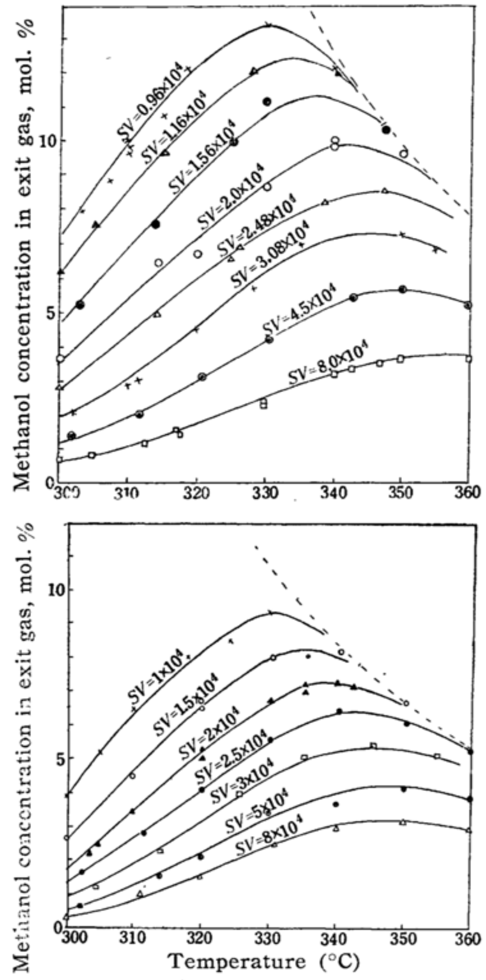


Fig. 1. Reactor.
A, thermocouple well: B, quartz tube: C, D and E, copper tubes: F, copper granules: G, catalyst: H, lead for heater.

The reactor is illustrated in Fig. 1. The catalyst (a packed bed of 22 mm. diameter and 17 mm. high) was pretreated for six hours at 350°C with a mixture of the gas (two moles of hydrogen and one mole of carbon monoxide) at atmospheric pressure, and thereafter the reactor was once brought to a lower temperature. At this lower temperature the gas was admitted at a space velocity at a high pressure, and then the temperature was raised gradually up to 330—340°C. After two hours' synthesis at this high temperature, a stationary conversion could be attained, and the temperature was then brought to the desired levels. During the synthesis the temperature difference along the catalyst bed remained less than 1°C.

Quantities of nitrogen such as 7.9% and 2.9% were contained in the feed gases of H_2/CO ratios of 2 and 3,74 respectively. Hydrogen, carbon monoxide and carbon dioxide in the gas after the synthesis were determined by the conventional methods; hardly any methane or olefine were



Figs. 2, 3. Methanol concentration as function of reaction temperature at different space velocities. 150 kg./cm^2. Fig. 2, H_2/CO $=2$: Fig. 3, $H_2/CO=6$

[*1] The concentration could also be determined from the quantity of methanol actually obtained in the synthesis. The value agreed well with that calculated by the above method.

detected. The liquid product was analyzed for water by Karl-Fischer's method and for methyl formate and formaldehyde by the procedures described in our previous paper⁶⁾.

The catalyst used in this study was a zinc oxide-chromia catalyst which was prepared from an intimate mixture of commercial zinc oxide (grade, pure) and aqueous solution of chromic acid. The mixture was dried in air at room temperature, and the resulting cake was powdered and pressed to tablets. The catalyst contained 19 wt. % chromia.

Results

Methanol Concentration as a Function of Temperature. — A part of the experimental results are shown in Figs. 2 and 3. In the figures, the methanol concentration in the exit gas in the synthesis at 150 kg./cm^2 are plotted as a function of temperature for each space velocity. Fig. 2 refers to the results with the gas of H_2/CO ratio of 2, and Fig. 3 to those with the gas of H_2/CO ratio of 6.

As is seen in Table I, the product contained water, methylformate and formaldehyde as by-products; and a little increase in carbon dioxide was found in the exit gas. However, it may reasonably be expected that the methanol concentration calculated by the above mentioned method is correct, because quantities of the by-products are very small.

TABLE I

IMPURITIES IN PRODUCT AND CARBON DIOXIDE CONTENT IN EXIT GAS

Reaction temperature, °C	By-products, wt. %			CO_2 in exit gas, vol. %
	H_2O	HCO_2CH_3	HCHO	
300	1.07	0.13	0.05	0.4
320	0.55	0.20	0.16	0.4
340	0.75	0.13	0.11	0.4
360	1.04	0.20	0.11	0.6

Every experiment was made at 150 kg./cm^2 at SV_0 of 1×10^4 with the gas of $H_2/CO=2$. The gas contained 0.2 vol. % of CO_2.

Equilibrium Constant for Methanol Synthesis.—The equilibrium constant of the methanol synthesis was determined by many workers,¹⁾⁷⁻¹⁴⁾ and the thermodynamical calculation was given by R. H. Ewell¹⁵⁾. However, there were some discrepancies among the values. In the present study an attempt has been made to obtain the equilibrium constant K by conducting the synthesis at a low space velocity at relatively high temperatures. The results*² are given in Fig. 4, in comparison with the results reported by the above investigators. The values obtained here are intermediate between Newit's and Ewell's. The values of the equilibrium constant on the straight line drawn through our observed values will be employed in our kinetic interpretation of the experimental data. The line runs parallel to Ewell's.

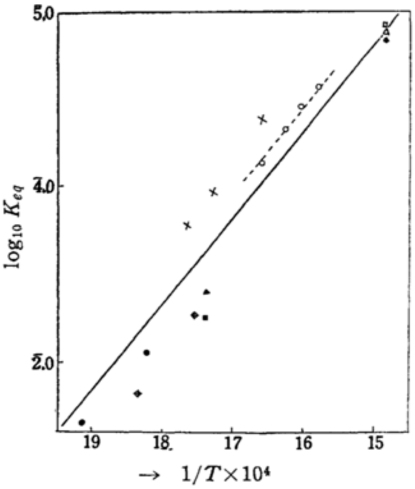


Fig. 4. Equilibrium constant for methanol synthesis.
×, Newit, Byrne and Strong: ○, the present authors: □, Lewis and Frolich: △, Brown and Galloway: ⊙, Audibert and Raineau: ▲, Smith and Hirst: ■, Smith and Branting: ⊕, Wettberg and Dodge: ●, Newton and Dodge: full line, Ewell.

Relations of Total Pressure to Methanol Concentration and Conversion Efficiency.—Changes in the methanol concentration and in the conversion efficiency (actual methanol concentration/equilibrium methanol concentration) with the total pressure are exemplified in Figs. 5 and 6 for the syntheses at 310 and 330°C

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7) D. M. Newit, B. J. Byrne et al., *Proc. Roy. Soc.*, **123**, 236 (1929).

8) L. Brown and A. E. Galloway, *Ind. Eng. Chem.*, **20**, 960 (1928).

9) E. Audiert and A. Raineau, ibid., **20**, 1105 (1928).

10) D. F. Smith, L. L. Hirst et al., ibid., **22**, 1037 (1930).

11) D. F. Smith and B. F. Branting, *J. Am. Chem. Soc.*, **51**, 129 (1929).

12) E. F. Wettberg and B. F. Dodge, *Ind. Eng. Chem.*, **22**, 1040, (1930).

13) R. H. Newton and B. F. Dodge, *J. Am. Chem. Soc.*, **56**, 1287 (1934).

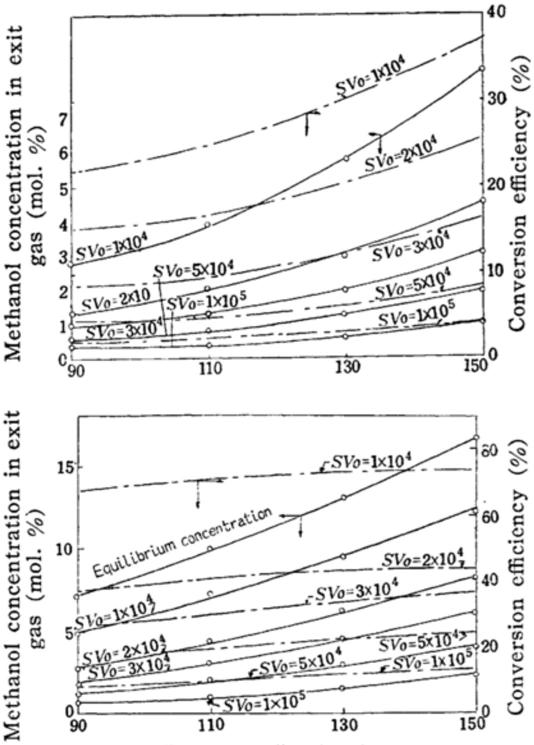
14) A. Tomita, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zassi)*, **54**, 504 (1951).

15) R. H. Ewell, *Ind. Eng. Chem.*, **32**, 147 (1940).

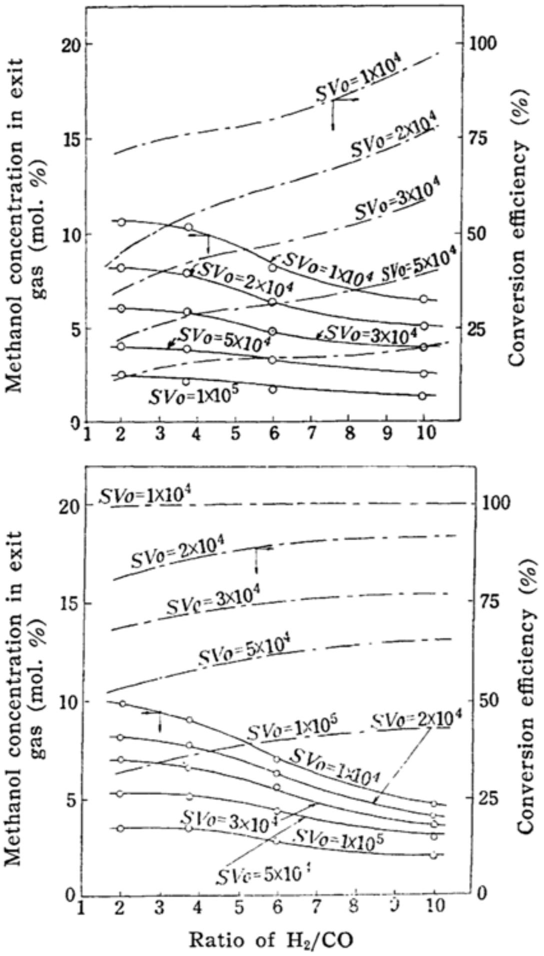
*2 Deviation of the pressure-concentration relation from the ideal gas law was corrected by means of the activity coefficient derived from Berthelot's formula (refer to R. H. Ewell¹⁵⁾).

with a gas-mixture containing two moles of hydrogen and one mole of carbon monoxide. The conversion efficiency tends to change with the total pressure more remarkably at the lower temperature but less so at the higher temperature. At the high temperature of 350°C it becomes nearly constant independent of the total pressure.

Dependence of the Methanol Concentration and the Conversion Efficiency on the Ratio of Hydrogen to Carbon Monoxide. —Figs. 7 and 8 show the plots of methanol concentration and of the conversion efficiency, vs. the ratio H_2/CO, respectively. At high ratios, the methanol concentration remains small, but it increases rapidly, at first, with the decreasing ratio, and then slowly at a ratio less than four. This increasing tendency appears less marked in the synthesis at higher space velocities where the concentration remains far below the equilibrium value. So far as the ratio is limited to a range from 2 to 4, it is expected that in the industrial synthesis, where the space velocity is relatively high and consequently the methanol concentration remains considerably lower than the equilibrium value, the space-time-yield will remain nearly the same, independent of the change in the ratio. At high ratios, the conversion efficiency is high, and tends to decrease monotonously as the ratio lowers to the value of two.



Figs. 5, 6. Methanol concentration and conversion efficiency as function of pressure at different space velocities.
full line, methanol concentration: dotted and dashed line, conversion efficiency.
$H_2/CO=2$, Fig. 5, 310°C: Fig. 6, 330°C



Figs. 7, 8. Methanol concentration and conversion efficiency as function of H_2/CO ratio.
full line, methanol concentration: dotted line, conversion efficiency. Fig. 7, 330°C: Fig. 8, 350°C

Discussion

Rate Equation of Methanol Synthesis. —In contrast to the rate equation by Natta et al., which was derived on the assumption of Langmuir's adsorption isotherm of the reactants and product on the catalyst, the rate equation presented here has been derived on the assumption of the logarithmic adsorption isotherm. The procedure of the derivation is analogous to that made by Temkin et al.[16] with their rate equation of the ammonia synthesis. It is assumed, however, that the desorption of methanol is rate determining and that neither the adsorption of hydrogen nor that of carbon monoxide is rate determining*3.

Based on the foregoing assumption, the rate of the methanol synthesis is given by

$$r = V_{des} - V_{ads} = k'_d e^{h\theta} - k'_a p_{CH_3OH} e^{-g\theta} \qquad (1)$$

where h and g are constants, θ is the degree of coverage with methanol, and k'_d and k'_a are constants at a definite temperature. On the other hand, it follows from the assumption that the adsorption isotherm must satisfy the equation:

$$\theta = \frac{1}{f} \ln a_0 p_{CH_3OH} \qquad (2)$$

where $f (f=g+h)$ is a constant and a_0 is a coefficient dependent only on temperature. To eliminate θ, $p^*_{CH_3OH}$ is introduced by following the manner of Temkin et al.,

$$\theta = \frac{1}{f} \ln a_0 p^*_{CH_3OH} \qquad (3)$$

$$p^*_{CH_3OH} = K \cdot p_{CO} p^2_{H_2} \qquad (4)$$

where K is the equilibrium constant of reaction and $p^*_{CH_3OH}$ is the fictitious methanol pressure in equilibrium with the degree of coverage θ. Hence the substitution of (3) and (4) in equation (1) gives the rate equation of the methanol synthesis.

$$\begin{aligned} r &= k_d (p_{CO} p^2_{H_2})^{1-\alpha} - k_a p_{CH_3OH} \cdot (p_{CO}\, p^2_{H_2})^{-\alpha} \\ &= k_d \{ (p_{CO} p^2_{H_2})^{1-\alpha} \\ &\quad - p_{CH_3OH} \cdot (p_{CO} p^2_{H_2})^{-\alpha} / K \} \qquad (5) \end{aligned}$$

where α is g/f.

The reaction rate of the methanol synthesis in a steady-state flow system through a fixed catalyst bed is usually given by equation (6),

$$r = c \cdot \frac{1}{(1+2z)^2} \cdot \frac{dz}{d(1/SV_0)} \qquad (6)$$

in the equation, c is a constant equal to $1/273 \cdot \boldsymbol{R} \cdot c_m$, where $\boldsymbol{R}$ is the gas constant and c_m is the mean compressibility coefficient of a gas at normal state, SV_0 is the space velocity based on the inlet side of the reactor, and z is the methanol concentration (mol. %) in the exit gas. The term $1/(1+2z)^2$ comes from the change in number of moles of the components of the system $2H_2 + CO \rightleftarrows CH_3OH$.

By combining equation (5) with equation (6) and integrating the resulting equation, equation (7) is obtained,

$$k/SV_0 = \int_0^z \frac{dz}{(1+2z)^2 \{ (p_{CO} p^2_{H_2})^{1-\alpha} - p_{CH_3OH} \cdot (p_{CO} p^2_{H_2})^{-\alpha} / K \}} \qquad (7)^{*4}$$

where k, the rate constant, is given by $k = 273 \cdot R \cdot c_m k_d$. The equation involves a constant α besides k. The constant α is here evaluated by the trial and error procedure as follows: since the integral term in equation (7) can be solved numerically for arbitrary values of z and α, the three values, 0.1, 0.3, and 0.7, were chosen for α and the integration was performed*5. The values of the integral thus obtained are plotted against the reciprocal space velocity which corresponds to the value of z employed in the integration. The equation postulates that whenever a correct value of α is chosen, the plots for the synthesis at a definite temperature at different pressures fall on one straight line passing through the origin. The postulate is well satisfied when the value of α is 0.3, as shown in Fig. 9. When α is 0.1 the plots for different pressures begin to diverge progressively with rising temperature, while when α is 0.7 they do so with lowering temperature. Moreover, the gradient of the straight line ($\alpha = 0.3$) gives the rate constant k.

The validity of our rate equation becomes established only when the rate constant is independent of the total pressure, the ratio of H_2/CO, and the space velocity. In Fig. 9 it has already been proved that the rate constant is independent of the total pressure so far as α is 0.3.

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16) M. Temkin and V. Pyzhev, *Acta Physicochim., U. S. S. R.*, **12**, 327 (1940).

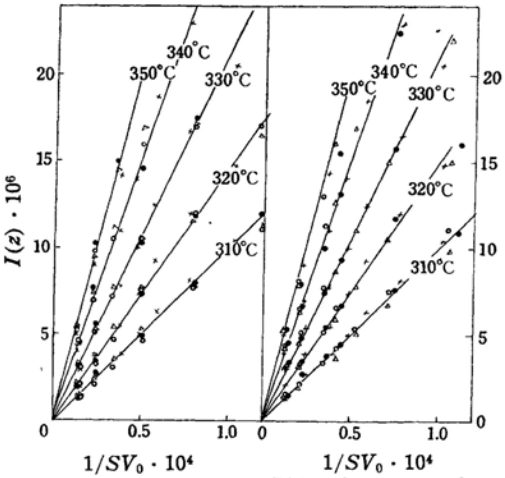
*3 This is because the premise that the adsorption of reactant is rate determining has proved to lead to a rate equation representing the results less satisfactorily. On the other hand, other steps such as the reaction between the adsorbed hydrogen and the adsorbed carbon monoxide might also be adopted as a rate determining step, but it will not be stated in this case, because the data could be explained by the concept written here.

*4 By introducing into equation (7) the following relations,

$a_{CH_3OH} = \gamma_{CH_3OH} \cdot Pz$, $a_{H_2} = \gamma_{H_2} \cdot 2p \cdot (n/2 - z)/(1+n)$,
$a_{CO} = \gamma_{CO} p \{1 + (1-n)z/(1+n)\}$, where a is the activity, γ is the activity coefficient, and p is the total pressure, the equation is rewritten as

$$K/SV_0 = \int_0^z \frac{\left[\gamma_{CO} \gamma^2_{H_2} \frac{4P^3 \{1+(1-n)z\}(n/2-z)}{(1+n)^3} \right]^{\alpha} \cdot dz}{(1+2z)^2 \left[\gamma_{CO} \gamma^2_{H_2} \frac{4P^3 \{1+(1-n)z\}(n/2-z)}{(1+n)^3} - \gamma_{CH_3OH} Pz/K \right]}$$

*5 M. Temkin et al., gave 0.5 for α in their derivation of the rate equation for the ammonia synthesis.



Figs. 9 and 10 Plots of $I(z)$ where $\alpha=0.3$ vs. reciprocal space velocity in the syntheses with gas of $n=2$ at different pressures (Fig. 9) and of different values of n at 150 kg./cm^2 (Fig. 10). Fig. 9, pressures (kg./cm^2): ×, 150: △, 130: ○, 110: ●, 90. Fig. 10, n (H_2/CO): ×, 2.0: ●, 3.74: △, 6: ○, 10.

As shown in Fig. 10, the variation in the ratio of H_2/CO causes hardly any change in the rate constant. Furthermore, the values of z at the different space velocities are calculated by employing a value of k and are plotted against the reciprocal space velocity in Fig. 11 (curves in full line). The curves agree well with the experimental data over a wide range of the space velocity.

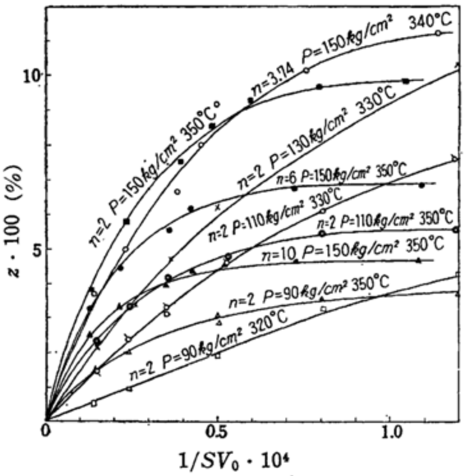


Fig. 11. Verification of the rate equation.

The plot of log k vs. reciprocal absolute temperature shows a straight line and the slope gives an apparent activation energy, 26.1 kcal./mol.

On the other hand, the rate equation which is the same in formula as equation (5) can also be obtained on the basis of Freundlich's adsorption isotherm (refer to the paper by T. Kwan[17]).

A rate equation of the methanol synthesis has already been proposed by Natta et al. on the basis of their very comprehensive experimental data on the synthesis. Their equation contains four constants, three of which are to be determined from the initial rate in three experiments performed at the same temperature, but at different total pressures and ratios of hydrogen to carbon monoxide. In the present work, however, accurate determination of the initial rate has been difficult, since the results do not contain so many values of the methanol concentration at very high space velocities as are sufficient for the drawing of the plot.

It is probable that by choice of suitable values for the constants, the rate equation by Natta et al. should represent the present experimental results well. However, the choice must be made by the trial and error method, and requires a tedious task of calculation.

Summary

Over a wide range of the total pressure and the ratio of hydrogen to carbon monoxide measurements on the methanol synthesis have been made at different temperatures at different space velocities. Relations of the total pressure to the methanol concentration and the conversion efficiency, and the dependence of the methanol concentration and the conversion efficiency on the ratio of hydrogen to carbon monoxide are presented.

Based on the assumption of the logarithmic adsorption isotherm and of the methanol desorption as the rate determining step, the rate equation for the methanol synthesis has been derived, which follows:

$$r=k_d\{(p_{CO}p^2_{H_2})^{0.7}-p_{CH_3OH}\cdot(p_{CO}p^2_{H_2})^{-0.3}/K\}$$

The equation has proved capable of representing our experimental results satisfactorily over relatively wide ranges of the pressures, the ratio of hydrogen to carbon monoxide and the space velocity.

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[17] T. Kwan, *J. Phy. Chem.*, **60**, 1033 (1956).