Reaction Rate of Water-Gas Shift Reaction[1]

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The rate equation plays the most fundamental role in the industrial application of gas phase catalytic processes. It gives us the information which is necessary for the design of the catalytic reactor as well as for the operation of the plant. For example, the optimum temperature distribution in a catalyst layer can be calculated for a given inlet gas composition and a given space velocity when the rate constants and the equilibrium constants of the reaction are known at every temperature[2]. Other sorts of useful knowledge, such as the temperature distribution in an adiabatic type reactor[3] and in a self-heat-exchanger-type reactor[4] and the optimum space velocity which gives the maximum space time yield in an adiabatic reactor[5], may also be predicted from the rate equation.

Water-gas shift reaction is one of the most important methods for producing hydrogen on an industrial scale. Therefore, the kinetical study of the water-gas shift reaction is very significant.

Padovani and Lotteri[6] and also Laupichler[7] presented the following as a rate equation:

$$-\frac{dP_{CO}}{dt}=k_1\{P_{CO}P_{H_2O}-K_pP_{CO_2}P_{H_2}\} \qquad (1)$$

In the process of an industrial-scale production of hydrogen, in which a large excess of water vapor is added to dry gas, the change in concentration of water vapor can be neglected during the course of reaction. Based on this fact, Laupichler derived the following equation as an approximation for Eq. (1).

$$-\frac{dP_{CO}}{dt}=k_1\{P_{CO}-\overset{\infty}{P}_{CO}\} \qquad (2)$$

Kal'kova and Temkin[8] gave a different equation

$$-\frac{dP_{CO}}{dt}=k_1\left\{P_{CO}\left(\frac{P_{H_2O}}{P_{H_2}}\right)^{\beta}-K_pP_{CO_2}\left(\frac{P_{H_2}}{P_{H_2O}}\right)^{1-\beta}\right\} \qquad (3)$$

where $\beta=0.45\sim0.55$.

This equation reproduces, according to the authors, the results of their experiments, which were made at relatively short contact times.

Reaction rates over a coprecipitated $Fe_2O_3-Cr_2O_3$ catalyst were followed in our laboratory[9] at also relatively short contact times and expressed by an equation different from Eq. (3), i.e.,

$$-\frac{dP_{CO}}{dt}=k_1\frac{P_{CO}P_{H_2O}-K_pP_{CO_2}P_{H_2}}{P_{CO_2}+KP_{H_2O}} \qquad (4)$$

All of the above mentioned studies[6,7,8,9] are unsatisfactory for industrial purposes in the following points. First, in all of the experiments stated above the inlet gas compositions were limited in very narrow ranges. And, in the studies of Kal'kova and Temkin[8] and in our laboratory[9], the contact times were far shorter than those used in industrial reactors. Moreover, the experimental verifications of these equations have been tried for only a very limited range of initial gas composition and space velocity.

The kinetics of reverse shift reaction is also one of the most interesting problems not only from an academic viewpoint, but also because of its industrial importance. As the reverse shift reaction occurs during the gasification of coal in industry, kinetical studies at high temperatures have been made by many investigators. On the other hand at relatively low temperatures reaction proceeds so slowly that very little has been known concerning the rate of reaction. Recently Barkley, Corrigan, Wainwright and Sands[10] followed the reaction rate by passing 1 : 4 to 4 : 1 mixtures of CO_2 and H_2 at 1000°F over

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[1] Part of this paper was presented at the 7th Annual Meeting of the Chemical Society of Japan, April 2, 1954.

[2] S. Kodama, K. Fukui, H. Tanaka and A. Mazume, *Chem. Eng.* (Japan), **15**, 85 (1951); P. H. Calderbank, *Chem. Eng. Progress*, **49**, 585 (1953); D. Annable, *Chem. Eng. Sci.*, **1**, 145 (1952).

[3] S. Kodama and K. Fukui, *Chem. Eng.* (Japan), **15**, 145 (1951).

[4] S. Kodama, K. Fukui and H. Tanaka, *J. Chem. Soc. Japan* (*Ind. Chem. Sec.*), **54**, 303 (1951); C. van Heerden, *Ind. Eng. Chem.*, **45**, 1242 (1953).

[5] S. Kodama, K. Fukui and A. Mazume, *Ind. Eng. Chem.*, **45**, 1644 (1953).

[6] C. Padovani and A. Lotteri, *J. Soc. Chem. Ind.*, **56**, 391T (1937).

[7] F.G. Laupichler *Ind. Eng. Chem.*, **30**, 578 (1938).

[8] N. B. Kal'kova and M. I. Temkin, *Zhur. Fiz. Khim.*, **23**, 695 (1949); *Chem. Abstr.*, **43**, 7308 (1949).

[9] S. Kodama, K. Fukui, T. Tame and M. Kinoshita, *Catalyst* (Japan), **8**, 50 (1952).

[10] L. W. Barkley, T. E. Corrigan, H. W. Wainwright and A. E. Sands, *Ind. Eng. Chem.*, **44**, 1066 (1952).

Fe_2O_3—CuO catalyst at different flow rates and derived the following rate equation,

$$\frac{dP_{CO}}{dt}=k_2\frac{P_{CO_2}P_{H_2}-\frac{1}{K_p}P_{CO}P_{H_2O}}{1+KP_{CO}+K'P_{CO_2}} \qquad (5)$$

But they did not make sure if this equation holds also in the water-gas shift reaction.

Under the circumstances mentioned above, it may be significant to obtain a rate equation of water-gas shift reaction which would be at least both accurate and practically useful for designing reactors. At the same time, it is of interest to ascertain that the rate expression obtained for the water-gas shift reaction would also be fit for the reverse shift reaction with the opposite sign, as it should be theoretically. Both the reactions were kinetically studied over a wide range of space velocity and inlet gas composition.

Experimental

Experiments were made by flow method at atmospheric pressure. Schematic flow diagrams of the apparatuses for the forward and the reverse reaction are shown in Figs. 1 and 2, respectively.

Carbon dioxide and hydrogen were taken from cylinders. Carbon monoxide was generated by dehydration of formic acid. These gases were purified by the usual methods.

The industrial catalyst used was of the composition shown below:

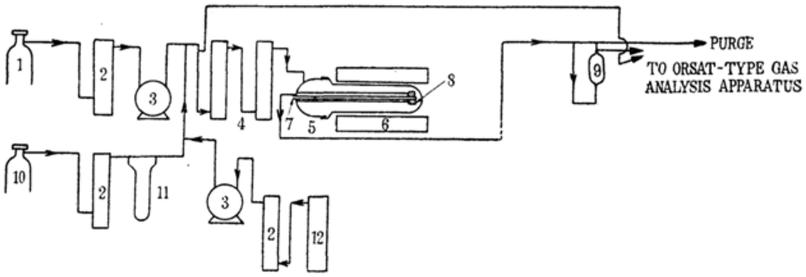
Fe_2O_3	72.25 (wt. %)	MgO	4.69 (wt. %)
Al_2O_3	12.55 (")	K_2O	1.53 (")
Cr_2O_3	7.46 (")		

The particle size of the catalyst was ranging in diameter from 10 to 20 Tyler mesh.

Flow rates of carbon monoxide and hydrogen were measured by a wet-type gas meter and that of carbon dioxide by an orifice-type flowmeter.

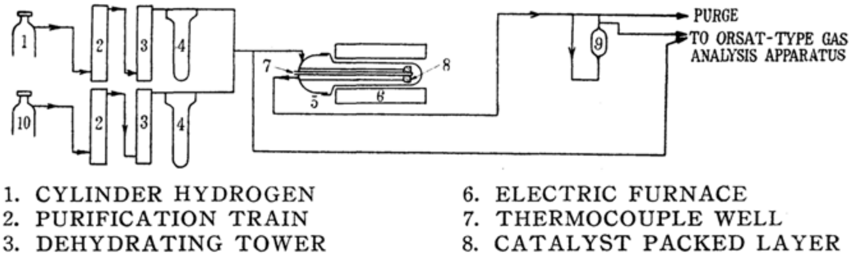
For water-gas shift reaction, inlet gas composition was determined from the analysis of dry gas and the saturation temperature with steam. For reverse shift reaction, inlet gas composition was calculated from the flow rates of carbon dioxide and hydrogen.

In the case of water-gas shift reaction dry gas was saturated with steam in a two-stage packed column kept at constant temperature. In order to prevent unsaturation, flow rates of dry gas were carefully kept at constant. The comple-



1. CYLINDER HYDROGEN
2. PURIFICATION TRAIN
3. WET-TYPE GAS METER
4. WATER SATURATOR (TWO-STAGE PACKED COLUMN)
5. SELF-HEAT-EXCHANGER-TYPE PYREX REACTOR
6. ELECTRIC FURNACE
7. THERMOCOUPLE WELL
8. CATALYST PACKED LAYER
9. GAS BURETTE
10. CYLINDER CARBON DIOXIDE
11. ORIFICE-TYPE FLOWMETER
12. CARBON MONOXIDE GENERATING APPARATUS

Fig. 1. Schematic flow diagram of the apparatus used for forward Reaction.



1. CYLINDER HYDROGEN
2. PURIFICATION TRAIN
3. DEHYDRATING TOWER
4. ORIFICE-TYPE FLOWMETER
5. SELF-HEAT-EXCHANGER-TYPE PYREX REACTOR
6. ELECTRIC FURNACE
7. THERMOCOUPLE WELL
8. CATALYST PACKED LAYER
9. GAS BURETTE
10. CYLINDER CARBON DIOXIDE

Fig. 2. Schematic flow diagram of the apparatus used for the reverse reaction.

teness of saturation was confirmed by preliminary experiments at each temperature.

In order to avoid the non-uniformity in the temperature distribution of the catalyst layer, a two-path-counter-current-type pyrex reactor[11] was used. Several reactors of different diameters were used for the experiments of different catalyst volumes, so that the packed length did not exceed 25 mm. and practically uniform temperature distribution was secured. The temperature of the catalyst layer was measured with a calibrated chromel-alumel thermocouple which was inserted in the bed.

Samples of both inlet and exit gas were analyzed with an Orsat-type gas analyzer. Most of the samples were analyzed for carbon dioxide, carbon monoxide and hydrogen.

Experimental Results

In Figs. 3, 4, 5, 6, 7, and 8 are shown the results for the water-gas shift reaction, plotted as the fractional conversions of carbon monoxide (Z) against contact times (t) for each investigated temperature and inlet gas composition. Fig. 9 shows the results of the reverse shift reaction by the plot of the

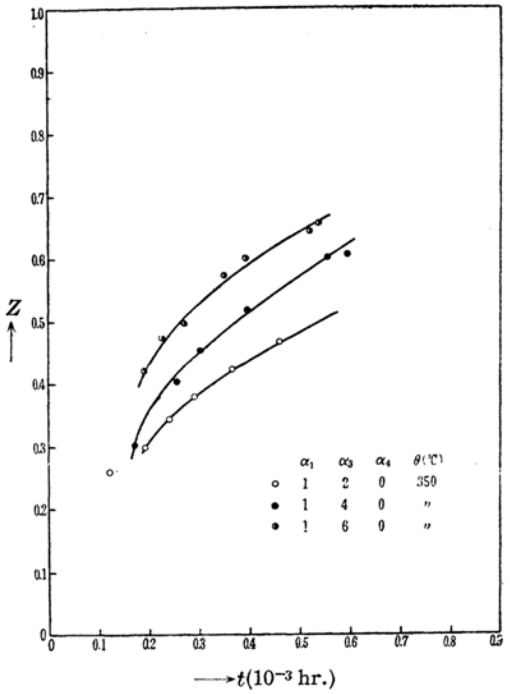


Fig. 4. Fractional conversion of carbon monoxide (Z) vs. contact time (t).

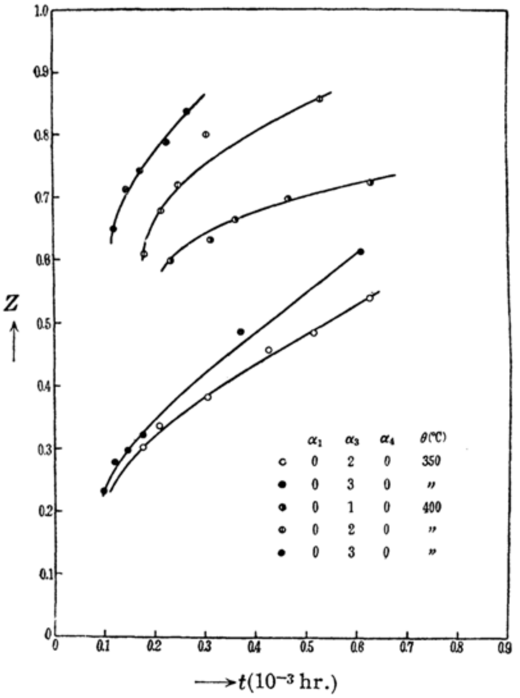


Fig. 3. Fractional conversion of carbon monoxide (Z) vs. contact time (t).

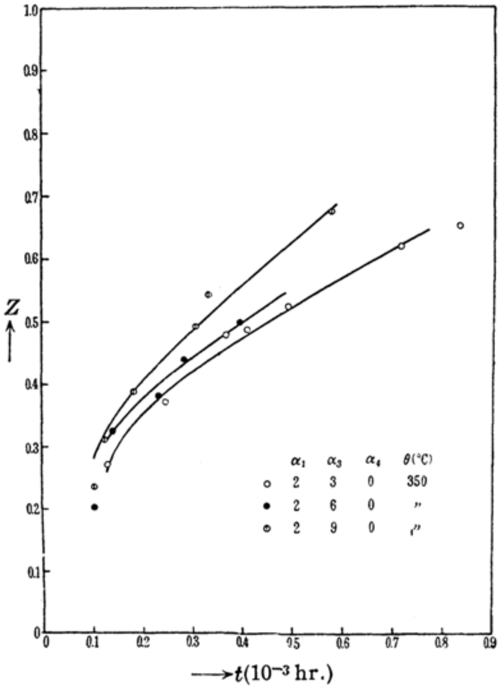


Fig. 5. Fractional conversion of carbon monoxide (Z) vs. contact time (t).

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[11] A. F. Farkas and H. W. Melville, "Experimental methods in gas reactions," Mac Millan and Co. Ltd., London, (1939) p. 305.

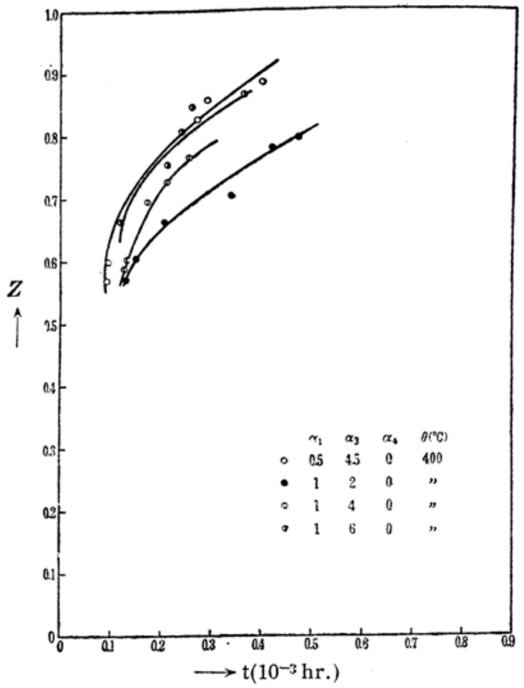

Fig. 6. Fractional conversion of carbon monoxide (Z) vs. contact time (t).

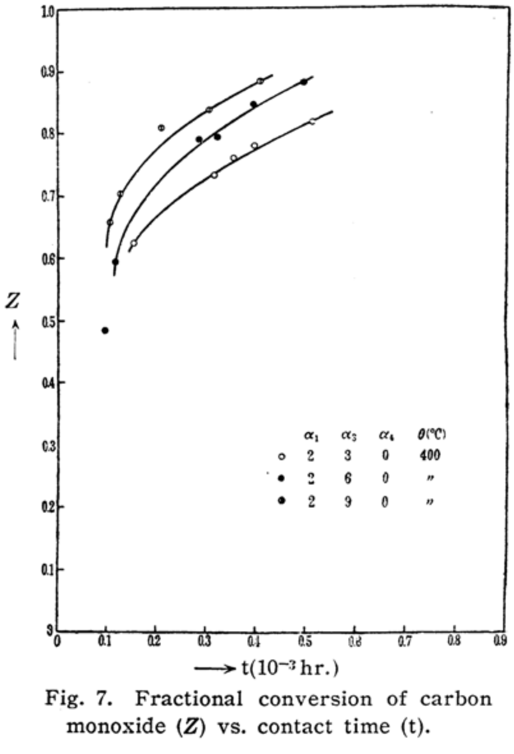

Fig. 7. Fractional conversion of carbon monoxide (Z) vs. contact time (t).

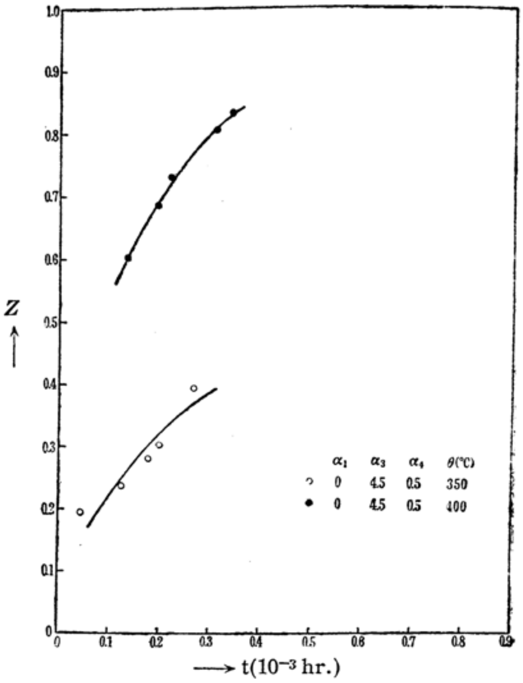

Fig. 8. Fractional conversion of carbon monoxide (Z) vs. contact time (t).

fractional conversions of carbon dioxide (Z') vs. contact times (t). The values of Z and Z' were calculated from the carbon dioxide content in the exit gas and the inlet gas composition, neglecting the side reaction, and t was calculated by the follwing equation.

$$t=\frac{\text{packed volume of catalyst (c.c.)}}{\text{total flow rate at each reaction temperature (c.c./hr.)}}$$

a) Water-Gas Shift Reaction.—In order to find the rate equation for the water-gas shift reaction which can reproduce the present results, many equations were put to the test, among which the following was proved to be most satisfactory.

$$-\frac{dP_{\mathrm{CO}}}{dt}$$

$$=k_1\frac{P_{\mathrm{CO}}P_{\mathrm{H_2O}}-K_{\mathrm{p}}P_{\mathrm{CO_2}}P_{\mathrm{H_2}}}{1+KP_{\mathrm{CO}}+K'P_{\mathrm{H_2O}}+K''P_{\mathrm{H_2}}+K'''P_{\mathrm{CO_2}}} \tag{6}$$

The partial pressure of the component i, P_i can be written in terms of fractional conversion and inlet gas composition, as

$$P_i=\frac{\alpha_i-\nu_i Z}{\sum_r \alpha_r}$$

where

$$\alpha_i=\frac{P^\circ{}_i}{P^\circ{}_{\mathrm{CO}}} \tag{7}$$

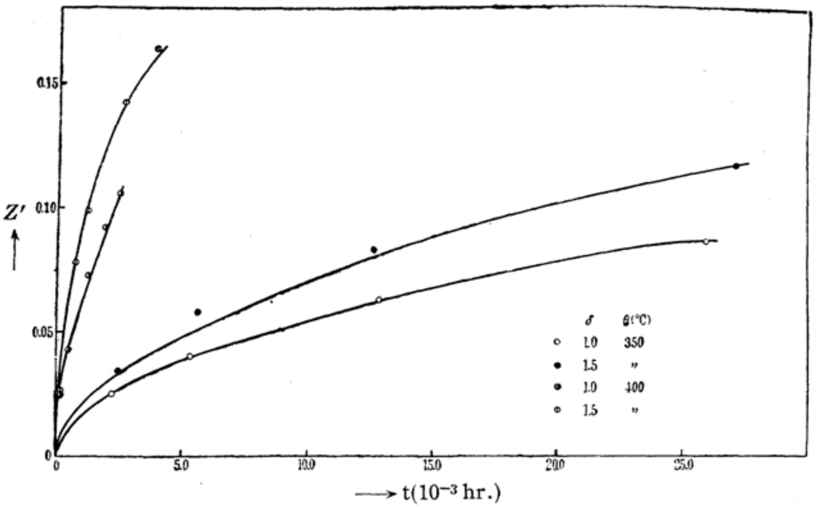

Fig. 9. Fractional conversion of carbon dioxide (Z') vs. contact time (t).

and ν_i represents the stoichiometric ratio of the component i in the forward reaction[8], i.e.,

$$\nu_{CO}=\nu_{H_2O}=1, \quad \nu_{CO_2}=\nu_{H_2}=-1$$

Using Eq. (7) the rate expression is represented as a function of Z and t. On integrating Eq. (6), the relation of Z and t is derived as follows:

$$\begin{aligned}P\frac{k_1t}{2.303}=\frac{1}{\beta-\gamma}\Big[&\{1+KP+\alpha_3(1+K'P)\\&+\alpha_1(1+K''P)+\alpha_4(1+K'''P)\\&+(K'''+K''-K'-K)P\beta\}\times\log\frac{\beta-Z}{\beta}\\&-\{1+KP+\alpha_3(1+K'P)+\alpha_1(1+K''P)\\&+\alpha_4(1+K'''P)+(K'''+K''-K'-K)P\gamma\}\\&\times\log\frac{\gamma-Z}{\gamma}\Big]\end{aligned}\tag{8}$$

where β and γ are the positive and negative roots of the following equation, respectively.

$$\begin{aligned}(1-K_p)Z^2-\{K_p(\alpha_1+\alpha_4)+(\alpha_3+1)\}Z\\+(\alpha_3-K_p\alpha_1\alpha_4)=0\end{aligned}\tag{9}$$

Table I shows the values of k_1 calculated

TABLE I

VALUES FOR k_1 (atm.$^{-1}$ hr.$^{-1}$ Unit)

(1) $\theta=350$, $K=0.3$ (atm.$^{-1}$), $K'=1.5$ (atm.$^{-1}$), $K''=4$ (atm.$^{-1}$), $K'''=20$ (atm.$^{-1}$)

$\alpha_1=0,\ \alpha_3=2,\ \alpha_4=0$		$\alpha_1=0,\ \alpha_3=3,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.176	1.048	0.0982	1.016
0.207	0.890	0.113	1.039
0.308	0.970	0.144	1.036
0.424	0.949	0.175	1.022
0.515	0.881	0.373	0.936
0.626	0.972	0.611	0.974

$\alpha_1=1,\ \alpha_3=2,\ \alpha_4=0$		$\alpha_1=1,\ \alpha_3=4,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.145	1.745	0.171	1.050
0.191	1.679	0.258	1.078
0.239	1.673	0.300	1.135
0.289	1.441	0.395	1.091
0.365	1.649	0.555	1.070
0.457	1.516	0.595	0.977

$\alpha_1=1,\ \alpha_3=6,\ \alpha_4=0$		$\alpha_1=2,\ \alpha_3=3,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.189	1.191	0.130	0.972
0.226	1.186	0.246	1.391
0.269	1.062	0.364	1.530
0.348	1.062	0.407	1.404
0.389	1.011	0.491	1.366
0.520	0.909	0.713	1.355
0.537	0.914	0.831	1.294

$\alpha_1=2,\ \alpha_3=6,\ \alpha_4=0$		$\alpha_1=2,\ \alpha_3=9,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.105	0.920	0.106	1.025
0.140	1.224	0.151	1.049
0.228	0.959	0.183	1.159
0.282	0.909	0.308	0.996
0.392	0.864	0.331	1.080
		0.574	0.985

$\alpha_1=0,\ \alpha_3=4.5,\ \alpha_4=0.5$	
$t(10^{-3}$ hr.)	$k_1(10^4)$
0.044	1.149
0.126	1.220
0.178	1.079
0.200	1.065
0.268	1.168

(II) $\theta=400$, $K=0.1$ (atm.$^{-1}$), $K'=0.5$ (atm.$^{-1}$), $K''=2$ (atm.$^{-1}$), $K'''=10$ (atm.$^{-1}$)

$\alpha_1=0,\ \alpha_3=1,\ \alpha_4=0$		$\alpha_1=0,\ \alpha_3=2,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.233	4.450	0.181	4.132
0.311	4.258	0.215	4.187
0.360	4.453	0.249	3.713
0.466	4.442	0.305	4.432
0.630	3.635	0.527	3.358

$\alpha_1=0,\ \alpha_3=3,\ \alpha_4=0$		$\alpha_1=0.5,\ \alpha_2=4.5,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.120	3.162	0.0884	2.802
0.145	3.276	0.0921	2.932
0.172	3.126	0.272	2.471
0.224	3.002	0.290	2.551
0.313	2.788	0.400	2.217

$\alpha_1=1,\ \alpha_3=2,\ \alpha_4=0$		$\alpha_1=1,\ \alpha_3=4,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.130	4.000	0.125	2.552
0.149	4.215	0.131	2.578
0.205	4.028	0.173	2.583
0.342	2.907	0.209	2.590
0.414	3.622	0.255	2.358
0.470	4.132		

$\alpha_1=1,\ \alpha_3=6,\ \alpha_4=0$		$\alpha_1=2,\ \alpha_3=3,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.117	2.702	0.150	2.780
0.216	1.966	0.315	3.045
0.239	2.342	0.353	3.080
0.259	2.553	0.394	3.062
0.368	2.000	0.510	2.976

$\alpha_1=2,\ \alpha_3=6,\ \alpha_4=0$		$\alpha_1=2,\ \alpha_3=9,\ \alpha_4=0$	
$t(10^{-3}$ hr.)	$k_1(10^4)$	$t(10^{-3}$ hr.)	$k_1(10^4)$
0.095	2.156	0.107	2.323
0.116	2.480	0.126	2.758
0.284	1.970	0.211	2.614
0.319	1.924	0.304	1.860
0.392	1.970	0.407	1.740
0.496	2.047		

$\alpha_1=0,\ \alpha_3=4.5,\ \alpha_4=0.5$	
$t(10^{-3}$ hr.)	$k_1(10^4)$
0.135	2.618
0.195	2.379
0.220	2.456
0.313	2.412
0.344	2.468

by Eq. (8). The numerical values of K_p used were taken from Lewis and Randall's work[12] and K, K', K'', and K''' were chosen so that the value of k_1 becomes most satisfactorily constant at a given temperature.

Experiments were also made at 450°C for a wide range of inlet gas composition and contact time. But in this case Eq. (6) failed to reproduce the experimental results.

b) Reverse Shift Reaction.—If Eq. (6) reproduces the results of the water-gas shift reaction, the reaction rate of the reverse shift reaction must be given as:

$$\frac{dP_{CO}}{dt} = k_2 \frac{P_{CO_2}P_{H_2} - \frac{1}{K_p}P_{CO}P_{H_2O}}{1+KP_{CO}+K'P_{H_2O}+K''P_{H_2}+K'''P_{CO_2}} \tag{10}$$

As in the case of the forward reaction, also, the relation of Z' and t is derived for the reverse shift reaction from Eq. (10), as

$$P\frac{k_2t}{2.303} = \frac{1}{-\beta'+\gamma'}\Big\{[1+K'''P+\delta(1+K''P) + (K+K'-K''-K''')\beta'P]\log\frac{\beta'-Z'}{\beta'} - [1+K'''P+\delta(1+K''P) + (K+K'-K''-K''')\gamma'P]\log\frac{\gamma'-Z'}{\gamma'}\Big\} \tag{11}$$

where δ represents the mole ratio of hydrogen to carbon dioxide at inlet, and β' and γ' are the positive and negative roots of the following equation, respectively.

$$(1-Z')(\delta-Z') - \frac{1}{K_p}Z'^2 = 0 \tag{12}$$

Calculated values of k_2 for all the experimental conditions are tabulated in Table II. The values of K, K', K'', K''' and K_p used for computing are the same as those used in the calculation for k_1.

TABLE II

VALUES FOR k_2 (in atm.$^{-1}$ hr.$^{-1}$ Unit)

(I) $\theta=350$, $K=0.3$ (atm.$^{-1}$), $K'=1.5$ (atm.$^{-1}$) $K''=4$ (atm.$^{-1}$) $K'''=20$ (atm.$^{-1}$)

$\delta=1.0$		$\delta=1.5$	
$t(10^{-3}$ hr.)	$k_2(10^2)$	$t(10^{-3}$ hr.)	$k_2(10^2)$
2.23	5.381	2.505	5.164
5.35	5.056	5.680	5.482
12.86	5.170	12.65	5.241
25.97	5.203	27.22	5.129

(II) $\theta=400$, $K=0.1$ (atm.$^{-1}$), $K'=0.5$ (atm.$^{-1}$), $K''=2$ (atm.$^{-1}$), $K'''=10$ (atm.$^{-1}$)

$\delta=1.0$		$\delta=1.5$	
$t(10^{-3}$ hr.)	$k_2(10^3)$	$t(10^{-3}$ hr.)	$k_2(10^3)$
0.175	2.067	0.128	1.925
0.403	2.078	0.749	2.097
1.242	1.915	1.224	1.966
1.890	1.943	2.660	1.956
2.534	1.985	3.924	1.890

Discussion

As seen from Tables I and II, the constancy of k_1 and k_2 is fairly good, which reveals the fact that the rate equations (6) as well as (10) are sufficiently accurate at least for the practical purpose.

Namely, the values of k_1 given in Table I are sufficiently constant over the contact time range 0.1–0.8×10^{-3} hr. and various inlet gas compositions at 350°C. At 400°C, k_1 varies somewhat with P°_{CO}. This change in k_1 may reasonably be attributed to the occurrence of the catalytic decomposition of carbon monoxide. However, at relatively small

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[12] G. N. Lewis, and M. Randall, "Thermodynamics and free energy of chemical substances," Mc Graw Hill Book Co., New York, (1923) p. 574.

P°_{CO}, as in the case of industrial reactors, the dependence of k_1 upon P°_{CO} is negligibly small, so that Eq. (6) may be useful for the reactor design.

Eqs. (1), (2), and (4) may be derived through some simplifications from Eq. (6), but Kalkova and Temkin's equation may not. Eq. (6) is similar to that of Horiuchi[13], derived theoretically.

Within the range of experimental error, no systematic deviation of the rate constants k_2 can be found from Table II. As is seen from these data, it is evident that Eq. (10) reproduces the rate data well.

Equilibrium constants K_p at 350°C and 400°C are calculated from k_1 and k_2. These values of K_p are shown in Table III together with those previously presented. The values of k_1 at 400°C used in calculating K_p are the average of k_1's obtained at relatively small P°_{CO}. The present values of K_p are in good agreement with previous publications, especially with values obtained by the direct method[14]. Eq. (6) may suggest something to us concerning the reaction mechanism, but no direct evidence for it has been given. It may rather be stressed that Eq. (6) serves as an empirical equation which is useful for industrial purposes.

TABLE III

VALUES FOR K_p

θ(°c)	K_p	
350	0.041	Neumann and Kōhler[14]
	0.0471	Lewis and Randall[12]
	0.0474	Kodama, Mazume, Fukuba and Fukui
400	0.0734	Engels[a]
	0.080	Neumann and Köhler[14]
	0.0824	Lewis and Randall[12]
	0.0796	Kodama, Mazume, Fukuba and Fukui

a) Engels, Dissertation, (1911) Karlsuhe (Cited in Reference 14).

Conclusion

The conclusion is as follows:

A rate equation for the water-gas shift reaction as well as for the reverse shift reaction which can reproduce the experimental results at 350°C and 400°C for various inlet gas compositions and contact times is obtained.

The equation seems to be sufficiently accurate at least for industrial purposes.

The assistance of Mr. T. Okada and Mr. M. Okazaki are gratefully acknowledged. Also the authors are indebted to The Befu Chemical Co. Ltd., for liquefied carbon dioxide.

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[13] J. Horiuti, *Catalyst* (Japan) 8, 58 (1952).

[14] B. Neumann and G. Köhler, *Z. Elektrochem.*, 34, 218 (1928).

k_1, k_2, K, K', K'', K'''=constants in the rate equation, which are function of temperature only.

K_p=equilibrium constant of the water-gas reaction

$$=\frac{P^{\infty}_{CO}\ P^{\infty}_{H_2O}}{P^{\infty}_{H_2}\ P^{\infty}_{CO_2}}$$

P_i=partial pressure of component i, atmospheres.

P=total pressure atmospheres.

t=contact time measured at reaction temperature, hours.

Z=fractional conversion of carbon monoxide for the forward reaction.

Z'=fractional conversion of carbon dioxide for the reverse reaction.

α_i=mole ratio of component i to carbon monoxide in feed of the forward reaction ($\alpha_2=1$).

δ=mole ratio of hydrogen to carbon dioxide in feed of the reverse reaction.

θ=temperature, °C.

Subscripts 1, 2, 3 and 4 designate hydrogen, carbon monoxide, water and carbon dioxide, respectively.

Superscript ∞ designates equilibrium conditions.

Superscript 0 designates inlet conditions.