

The Kinetics of the Water Gas Conversion at Atmospheric Pressure

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The kinetics of the water gas conversion $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ at atmospheric pressure over an iron oxide-chromium oxide catalyst has been investigated in the temperature range 330–500°C. The catalyst was "stabilized" by running for 10–14 days at working conditions before starting the measurements. It was found that the rate of the forward reaction could be expressed by an equation of the following exponential type, $\text{rate} = k (\text{CO})^l (\text{H}_2\text{O})^m (\text{CO}_2)^n$ where (CO), (H₂O) and (CO₂) are partial pressures of CO, H₂O and CO₂, respectively. The rate is independent of H₂ partial pressure. The exponents l , m , and n vary only slightly with temperature and are situated within the following ranges, $l = 0.80 - 1.00$, $m = 0.20 - 0.35$, and $n = -0.65$ to -0.50 . Preliminary values of l , m , and n were obtained at relatively low conversions by a graphic method. For the final testing and for testing at higher degrees of conversion the rate expression has been integrated by means of an electronic digital computer. By application of an "average" rate expression for the whole temperature range the apparent energy of activation has been determined to be 27.4 kcal/mole.

The water gas conversion $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ over iron oxide based catalysts is of considerable industrial importance. Although a number of more or less conflicting rate equations¹⁻⁸ have been put forward, a generally accepted kinetic expression does not exist.

The present work was undertaken as part of a program aiming at establishing data for calculation of required amounts of catalyst for industrial plants. This work will later also include experiments at elevated pressure. During the work described here an electronic calculating machine has been used for establishing rate equations.

EXPERIMENTAL

Gases. All gases employed, CO, N₂, H₂, and CO₂, were taken from cylinders. CO was about 98.5 % pure, the rest being mainly N₂ (about 1 %), H₂ (about 0.5 %), and O₂ (about 0.2 %). Further, traces of iron carbonyl could be found. CO₂ was less than 0.1 %. CO was purified by passing over Cu-wire at 320°C (which removes traces of oxygen and

of iron carbonyl present), alumina, potassium hydroxide pellets, and active carbon. N_2 and H_2 were purified in the same way. CO_2 was used without further purification.

Catalyst. The catalyst used was a commercial iron oxide-chromium oxide catalyst. Particle size was 0.8–1.2 mm. The amount of catalyst used has been either 3.00 g (unreduced) diluted by 9.5 cm³ inert material (quartz) of the same particle size, or 12.00 g diluted by 38.0 cm³ inert material. The total volume of catalyst and diluting material was 12.0 cm³ or 48.0 cm³, respectively. The height of the catalyst bed was 5.2 cm or 21.0 cm, respectively. Before starting the measurements, the catalyst was reduced, and thereafter stabilized (or "aged") by running for 10–14 days at working conditions and at the temperature at which the measurements were intended to take place. Catalyst samples used for the runs at temperatures below 380°C, however, were stabilized at 380°C. During the stabilization period a decrease of the activity occurred accompanied by an increase in pore size and a decrease in surface area. Even the stabilized catalyst was not completely stable in activity, but after the stabilization period further loss of activity was so slow as to permit measurements which will be useful for the calculation of industrial performance during a considerable period of time.

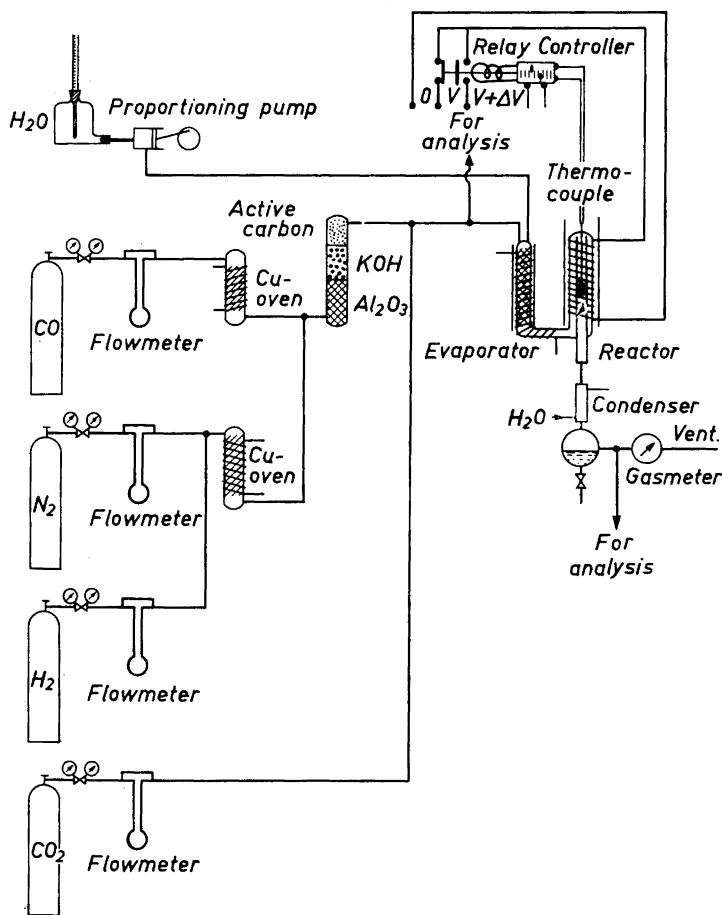


Fig. 1. Schematic drawing of experimental set-up.

Experimental set-up. A diagram of the experimental set-up is shown in Fig. 1. The gases were supplied through flowmeters and purification trains to the evaporator where liquid water was introduced by means of a proportioning pump. Mixture of water vapour and gases was passed through a heated tube to the glass reactor, which was constructed in the following way: The catalyst was placed in an inner tube, through which a thermocouple tube passed so that the temperature might be measured at any level of the catalyst layer. Incoming feed gas passed through an annular space in countercurrent flow with the gas in the catalyst tube. The outer wall of the annular space was provided with a Ni-chrome heating coil. Outside the heating coil was placed a glass mantle. By manipulating the insulation of this outer glass mantle it was possible to maintain almost isothermal conditions throughout the catalyst layer, the variation being at maximum 4°C between the warmest and the coldest spot. The thermocouple was ordinarily placed at a point having an average temperature. The temperature of the reactor was maintained by means of the thermocouple and a controller, which regulates the voltage of the heating coil. The calibration of the controller was controlled daily by means of a potentiometer.

Effluent gas passed through a condenser and a precision wet gas meter. Samples for analysis of exit gas could be taken out without changing the flow conditions in the reactor.

Analytical procedure. CO and CO₂ were determined in an Orsat apparatus by adsorption in KOH-solution and in CuCl-solution, respectively. H₂ was determined by gas chromatography. The rest of the gas was considered to be nitrogen. Between 3 and 6 analyses were made at each set of conditions. The figures given in the tables are average figures from these determinations.

LIST OF SYMBOLS

- F = total feed rate (mole/h).
 f = feed rate of CO (mole/h).
 k = reaction rate constant for forward reaction.
 K = equilibrium constant for the water gas conversion
 K_1, K_2, K_3, K_4 = overall constants appearing in eqns. (4), (6), (8), and (10), respectively.
 $l, m, n,$ and q = exponents occurring in the reaction rate equation (1).
 $(\text{CO}), (\text{H}_2\text{O}), (\text{CO}_2), (\text{H}_2)$ = partial pressures (atm.) of CO, H₂O, CO₂, and H₂, respectively. Subscript zero indicates initial partial pressure.
 r = net reaction rate (mole CO converted/(h) (g catalyst)).
 r_f and r_b = forward and backward reaction rates, respectively.
 x = degree of conversion of CO $\left(\frac{\text{moles CO converted}}{\text{moles CO in feed gas}} \right)$.
 W = weight of catalyst (g).

DEVELOPMENT OF A RATE EQUATION

Past experience has shown^{5,9,10} that it is generally possible to express the experimental results for a unidirectional rate by an equation of the type $r_f = k \cdot (A)^a \cdot (B)^b \cdot (C)^c \dots$ where (A), (B), (C), etc. are partial pressures of reactants and products. An exponential equation of this type is more simple to use than an equation of the Langmuir-Hinshelwood-Hougen-Watson type. As discussed in Refs.^{9,10} these two types of rate expressions can generally be approximated to each other.

For the present case a rate equation of the exponential type for the forward reaction is

$$f \cdot \frac{dx}{dw} = k \cdot (\text{CO})^l \cdot (\text{H}_2\text{O})^m \cdot (\text{CO}_2)^n \cdot (\text{H}_2)^q \quad (1)$$

Assuming the Horiuti stoichiometric number (*cf. e.g. Ref.*⁵) for the rate determining step to be one, the net rate is

$$r = r_i - r_b = k (\text{CO})^l \cdot (\text{H}_2\text{O})^m \cdot (\text{CO}_2)^n \cdot (\text{H}_2)^q \cdot (1 - \beta) \quad (1a)$$

$$\text{where } \beta = (\text{CO}_2)(\text{H}_2)/K(\text{CO})(\text{H}_2\text{O})$$

The experiments rapidly showed the rate to be independent of the hydrogen partial pressure in the whole temperature range 330°—500°, *i.e.* $q = 0$.

By substituting this and $f = F(\text{CO})_0$ in eqn. (1) we have

$$F \cdot \frac{dx}{dw} = k (\text{CO})_0^{l-1} (1-x)^l [(\text{H}_2\text{O})_0 - x \cdot (\text{CO})_0]^m [(\text{CO}_2)_0 + x(\text{CO})_0]^n \quad (2)$$

If $x \cdot (\text{CO})_0$ is small in comparison with $(\text{CO})_0$, $(\text{H}_2\text{O})_0$, and $(\text{CO}_2)_0$ an approximate integration leads to

$$x = (kW/F) \cdot (\text{CO})_0^{l-1} \left(1 - \frac{x}{2}\right)^l [(\text{H}_2\text{O})_0 - \frac{x}{2}(\text{CO})_0]^m [(\text{CO}_2)_0 + \frac{x}{2}(\text{CO})_0]^n \quad (3)$$

or, for constant F , $(\text{CO})_0$ and $(\text{H}_2\text{O})_0$,

$$\ln x = K_1 + n \cdot \ln [(\text{CO}_2)_0 + \frac{x}{2}(\text{CO})_0] \quad (4)$$

i.e., by plotting

$$\ln x \text{ vs. } \ln [(\text{CO}_2)_0 + \frac{x}{2}(\text{CO})_0]$$

for varying $(\text{CO}_2)_0$ and small conversions n is obtained as the slope of a straight line if an equation of the type (1) is fulfilled. If $(\text{CO}_2)_0 = 0$ and $x \cdot (\text{CO})_0$ is small in comparison with $(\text{CO})_0$ and $(\text{H}_2\text{O})_0$, (2) may be approximatively integrated to:

$$x^{-n+1} = (-n+1)(kW/F) \cdot (\text{CO})_0^{n+l-1} \left(1 - \frac{x}{2}\right)^l [(\text{H}_2\text{O})_0 - \frac{x}{2}(\text{CO})_0]^m \quad (5)$$

or for constant F and $(\text{H}_2\text{O})_0$

$$(-n+1) \ln x = K_2 + (n+l-1) \ln \left[(\text{CO})_0 \cdot \left(1 - \frac{x}{2}\right)^{l/(n+l-1)} \right] \quad (6)$$

By applying the above value of n and choosing an approximate value of l (for calculation of the term $\left(1 - \frac{x}{2}\right)^{l/(n+l-1)}$ which varies only slightly) and then plotting

$$\ln x \text{ vs. } \ln \left[(\text{CO})_0 \left(1 - \frac{x}{2}\right)^{l/(n+l-1)} \right]$$

for varying $(\text{CO})_0$, a straight line should be obtained the slope of which is $(n + l - 1)/(-n + 1)$ or

$$l = (1 - n) + (1 - n) \times \text{slope} \quad (7)$$

If $(\text{CO}_2)_0 = 0$ and F and $(\text{CO})_0$ are constant one obtains instead of (6)

$$(-n + 1) \ln x = K_3 + m \ln \left\{ [(\text{H}_2\text{O})_0 - \frac{x}{2} (\text{CO})_0] \left(1 - \frac{x}{2} \right)^{l/m} \right\} \quad (8)$$

By inserting an approximate value of m and making a logarithmic plot, a straight line should again be obtained, the slope of which is $m/(-n + 1)$ or

$$m = (-n + 1) \times \text{slope} \quad (9)$$

Finally it has also in some cases been of interest to determine l by varying the partial pressure of CO in feed gas while maintaining constant essential partial pressures of both CO_2 and H_2O . In this case eqn. (3) is transformed into

$$\ln \left[x \left(1 - \frac{x}{2} \right)^l \right] = K_4 + (l - 1) \ln (\text{CO})_0 \quad (10)$$

and $l - 1$ is obtained as the slope of a straight line.

EVALUATION OF EXPERIMENTAL RESULTS

The procedure for obtaining the experimental data has been the following. At each of the temperatures 330°C, 380°C, 420°C, 460°C, and 500°C 4 or 5 series of runs have been made varying the partial pressure of one of the four components CO, H_2O , CO_2 , and H_2 during each series without changing other variables. The balance partial pressure has been maintained by means of nitrogen, which is supposed not to influence the reaction.

At 360°C only a single series of runs has been made during which the CO-concentration has been varied while a constant CO_2 -concentration has been maintained in the feed gas.

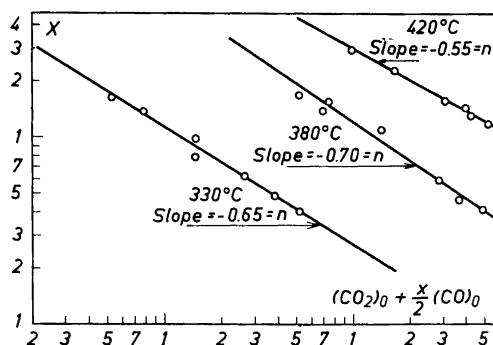


Fig. 2. Determination of n at 330°, 380°, and 420°C according to eqn. (4) by plotting $\ln x$ vs. $\ln ((\text{CO}_2)_0 + \frac{x}{2} (\text{CO})_0)$. Experimental data are given in Tables 4, 8 and 13, respectively. The abscissa applied at 330°C is displaced one decade relatively to that applied at 380°C and 420°C.

The data obtained in this way at 330°C and 380°C have been plotted according to eqns. (4), (6), and (8) giving l, m , and n , respectively. Data obtained at 360°C, 380°C, and 420°C by varying the CO-concentration while keeping a constant CO₂-concentration have been plotted according to eqn. (10), giving l .

Further the data obtained at 420°C by varying the CO₂-concentration have been plotted according to eqn. (4), giving n . The other data obtained at 420°C and those obtained at higher temperatures have not been plotted, the conversions being too high.

The diagrams obtained by these plottings are shown in Figs. 2—5 and the values of l, m and n thus obtained are summarized in Table 1.

The correctness of the values of l, m , and n thus obtained has been controlled in the following way. An approximate value of k together with the above values of l, m , and n are inserted in the net rate equation (1a). This equation is then integrated for each set of the appropriate experimental conditions with the aid of an electronic digital computer (DASK) which directly prints the composition of the exit gas. The optimum values of the variables k, l, m , and n were found by trial and error in the following way. At the exit of the reactor an increase of the conversion Δx , is approximately proportional to an increase of the amount of catalyst ΔW for small values of Δx and ΔW . A fractional increase of W of $\Delta W/W$ is equal to a fractional increase of k of $\Delta k/k$. It is therefore possible by applying an approximate value of k and letting the computer print the gas composition at the exit and at a short distance before the exit to obtain by interpolation (or extrapolation) a value of k which makes the calculated value of x equal to the experimentally found value of x . l, m or n (depending upon which component is being varied) is varied until the values of k show no systematic variation within each series. If the average value of the k 's thus obtained is essentially different from that applied for the electronic calculation the latter is repeated using the average value. l, m , and n have only been varied in steps of 0.05. The data used for Figs. 2—4 have been treated in this way. It appeared that the graphically found values of l, m , and n were very nearly correct.

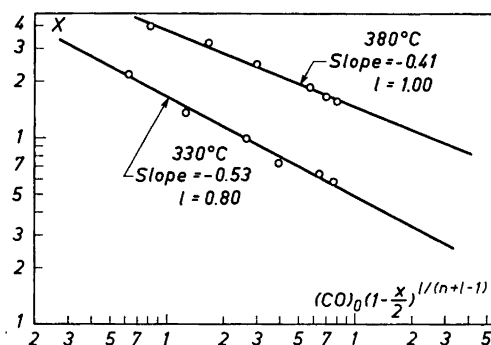


Fig. 3. Determination of l at 330° and 380° according to eqn. (6) by plotting $\ln x$ vs $\ln \left[(\text{CO})_0 \left(1 - \frac{x}{2} \right)^{l/(n+l-1)} \right]$. Experimental data are given in Tables 2 and 6.

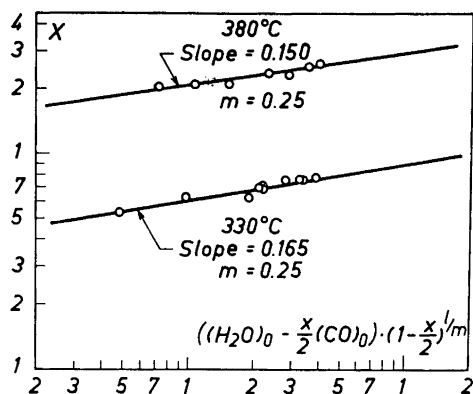


Fig. 4. Determination of m at 330° and 380° according to eqn. (8) by plotting $\ln x$ vs. $\ln \left\{ \left[(\text{H}_2\text{O})_0 - \frac{x}{2} (\text{CO})_0 \right] \left(1 - \frac{x}{2} \right)^{1/m} \right\}$. Experimental data are given in Tables 3 and 7.

At the conditions (higher temperatures) where the conversions obtained were too high to be plotted according to eqns. (4), (6), (8), and (10), it appeared, when applying the electronic computer, that only minor changes of the values obtained for l , m , and n at 380°C were necessary at these temperatures in order to obtain a constant value of k within each series.

In addition to the runs performed at constant space velocity and varying partial pressure of one of the components also a number of runs have been

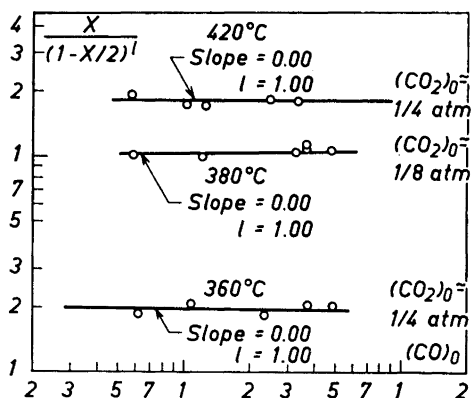


Fig. 5. Determination of l at 360°, 380°, and 420°C according to eqn. (10) by plotting $\ln \left[\frac{x}{\left(1 - \frac{x}{2} \right)^l} \right]$ vs. $\ln (\text{CO})_0$. Experimental conditions at 360°C: $(\text{H}_2\text{O})_0 \simeq (\text{CO}_2)_0 \simeq \frac{1}{2}$ atm., amount of catalyst 12.00 g, total feed gas $\simeq 2.4$ mole/h. At 380°: $(\text{H}_2\text{O})_0 \simeq \frac{3}{8}$ atm., $(\text{CO}_2)_0 \simeq \frac{1}{8}$ atm., amount of catalyst 3.00 g, total feed gas $\simeq 2.4$ mole/h. At 420°: $(\text{H}_2\text{O})_0 \simeq \frac{3}{8}$ atm., $(\text{CO}_2)_0 = \frac{1}{4}$ atm., amount of catalyst 3.00 g, total feed gas $\simeq 2.5$ mole/h. The ordinate applied at 360° is displaced one decade relatively to that applied at 380° and 420°.

Table 1. The values of l , m , and n obtained from Figs. 2—5.

	330°C	360°C	380°C	420°C
l (eqn. 6)	0.80		1.00	
l (eqn. 10)		1.00	1.00	1.00
m (eqn. 8)	0.25		0.25	
n (eqn. 4)	-0.65		-0.70	-0.55

made with constant feed gas composition and varying space velocity so that the rate equation has been tested over a considerable range of degrees of conversion. Such series of runs have been performed at 330, 380, 400, and 420°C.

As the exponent n is negative the feed gas concentrations cannot be directly fed to the electronic computer when $(\text{CO}_2)_0 = 0$. In these cases the gas composition has been calculated by hand at a distance of $\frac{1}{2}$ —1 % of the total bed length from the top, and these data have then been applied to the computer. This calculation can be made fairly accurately by approximate methods.

The results of the calculations are shown in Tables 2—20. The rate equation given above each table is that which has been applied for calculating the degree of conversion shown in column 8 by means of the electronic digital computer. Column 9 gives the experimentally found degrees of conversion, and the last column gives the value of k which by means of the above described interpolation method makes the calculated conversion equal to the experimentally found conversion.

Finally a series of runs has been made during which the temperature has been varied. The catalyst was stabilized at 500°C, and measurements have been made at 500, 460, 420, 380, 360, 330, and again 500°C. The results of these runs are shown in Table 22.

DISCUSSION

It is of importance to ascertain whether the experimental results have been influenced by transport restrictions.

Table 2. 330°C. Variation of $(\text{CO})_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction $r_f = 0.0050 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.388	74.80	0	0.56	0.04	24.60	5.67	5.8	0.0052
2	2.388	62.80	0	0.47	12.13	24.60	6.21	6.45	0.0053
3	2.383	37.70	0	0.28	37.52	24.50	8.05	7.3	0.0042
4	2.383	25.20	0	0.19	50.11	24.50	9.86	10.0	0.0051
5	2.379	12.00	0	0.09	63.11	24.80	14.31	13.6	0.0046
6	2.363	5.60	0	0.04	63.86	24.50	20.71	22.0	0.0055
Average									0.0050

Table 3. 330°C. Variation of $(\text{H}_2\text{O})_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.0048 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.279	50.70	0	0.38	22.92	26.00	7.00	7.0	0.0048
2	2.413	48.20	0	0.36	12.24	39.20	7.41	7.6	0.0050
3	2.321	49.40	0	0.37	24.23	26.00	7.02	7.05	0.0048
4	2.254	48.40	0	0.37	4.43	46.80	7.91	8.0	0.0049
5	2.283	48.20	0	0.36	11.44	40.00	7.68	7.55	0.0047
6	2.317	47.60	0	0.36	18.44	33.60	7.45	7.6	0.0050
7	2.333	47.10	0	0.35	26.35	26.20	7.18	7.0	0.0046
8	2.363	49.40	0	0.37	27.63	22.60	6.79	6.4	0.0043
9	2.254	50.40	0	0.38	36.62	12.60	6.27	6.3	0.0048
10	2.296	50.20	0	0.38	42.72	6.70	5.54	5.4	0.0046
Average									0.0048

A calculation by means of the method given by Hougen and Watson¹¹ shows that the external mass transfer to and from the geometrical surface is not of great importance at any of the experimental conditions used.

Internal diffusion in the catalyst pores is definitely not of importance at temperatures $\leq 380^\circ\text{C}$ as shown by calculation as well as by experiment (comparison of conversion obtained by 1 mm and by 2 mm particles, respectively). At higher temperatures the situation is somewhat more complicated. For runs at 420°C without CO_2 in the feed gas calculations by the method of Hoogschagen¹² gave an effectiveness factor of at least 90 %, which, if correct, would be satisfactory. However, during these calculations certain assumptions have been made (*e.g.*, first order reaction, spherical catalyst particles) which are not correct. It would therefore be possible that the effectiveness factor actually were smaller. However, the agreement between the value of l (1.00) obtained

Table 4. 330°C. Variation of $(\text{CO}_2)_0$. Amount of catalyst 12.00 g. Rate equation for forward reaction: $r_f = 0.0054 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.329	24.70	0	0.18	50.12	25.00	23.1	22.8	0.0052
2	2.288	25.50	25.50	0.15	23.55	25.30	6.05	6.3	0.0056
3	2.283	24.80	13.20	0.13	36.37	25.50	8.92	7.9	0.0047
4	2.392	24.00	51.00	0.08	0.92	24.00	3.79	4.0	0.0057
5	2.288	24.80	38.10	0.08	12.82	24.20	4.72	4.9	0.0056
6	2.267	25.00	5.83	0.08	43.89	25.20	13.26	14.0	0.0058
7	2.333	24.80	3.09	0.08	45.73	26.30	16.40	16.5	0.0055
8	2.271	25.70	13.10	0.08	36.72	24.40	8.83	9.9	0.0061
Average									0.0055

Table 5. 330°C. Variation of space velocity. Amount of catalyst 12.00 g. Rate equation for forward reaction $r_f = 0.0052 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.313	24.10	0	0.18	50.32	25.40	23.1	22.5	0.0050
2	1.125	23.90	0	0.18	49.22	26.70	34.2	33.3	0.0050
3	0.608	22.40	0	0.17	49.33	28.10	47.9	48.8	0.0054
4	4.704	24.70	0	0.19	48.91	26.20	15.45	15.6	0.0053
5	9.475	23.60	0	0.18	52.12	24.10	10.43	11.3	0.0059
Average									0.0053

from runs containing a constant high concentration of CO₂ in the feed gas (Fig. 5 and Table 1) and from runs without CO₂ in the feed gas (Table 11) — the rate of reaction being much higher in the latter case — strongly indicates that diffusion restriction does not seriously influence the value of l . A possible influence of diffusion on m is even less likely as the conversion varies only slightly with (H₂O)₀. For the determination of n the feed gas has contained so much CO₂ that the rate has been sufficiently low. There is therefore good reason to believe that the values of l , m , and n obtained at 420°C have not been influenced by diffusion restriction. At 460°C and 500°C a constant high concentration of CO₂ has been superimposed in all runs. This results in the reaction rate being so low, especially at 460°C, that diffusion is not of importance.

As discussed later there is a linear relationship between $\ln k$ and $1/T$, which also shows that diffusion restriction over the entire temperature range 330—500°C has not been of importance.

It has been mentioned above that each catalyst sample has been "stabilized" by running for about 10 days at the temperature at which the measurements were going to be made (except the catalyst samples used for runs at temperatures below 380°C which have been stabilized at 380°C). In spite of

Table 6. 380°C. Variation of (CO)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.0290 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.20}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.262	24.60	0	0.18	49.62	25.60	24.4	24.8	0.0299
2	2.213	12.00	0	0.09	61.41	26.50	32.0	32.4	0.0297
3	2.267	70.80	0	0.53	1.97	26.70	16.4	15.6	0.0265
4	2.213	49.70	0	0.37	22.83	27.10	19.1	18.8	0.0282
5	2.246	61.40	0	0.46	11.44	26.70	17.4	16.8	0.0272
6	2.221	6.00	0	0.04	66.96	27.00	40.3	39.3	0.0276
Average									0.0282

Table 7. 380°C. Variation of $(\text{H}_2\text{O})_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction $r_f = 0.0252 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.20}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.354	24.00	0	0.18	24.02	51.80	24.3	23.5	0.0237
2	2.238	23.00	0	0.17	0.93	75.90	26.5	26.8	0.0253
3	2.346	24.10	0	0.18	10.12	65.60	25.0	25.6	0.0263
4	2.192	24.10	0	0.18	34.52	41.20	24.6	23.9	0.0239
5	2.281	24.30	0	0.18	61.82	13.70	20.8	20.6	0.0248
6	2.263	25.20	0	0.19	54.91	19.70	21.7	21.1	0.0239
7	2.250	25.20	0	0.19	48.01	26.60	22.6	21.1	0.0222
Average									0.0243

this "stabilization" (or ageing) the activity of the catalyst is not completely stable (especially at higher temperatures) which may be seen when running a sample over long periods. As only one set of conditions has been investigated per day, and as one catalyst sample generally has been used for several series (although only at one temperature) each sample has in fact been in constant use for a period of the order of a few months. For this reason the rate constant k obtained at constant temperature may be seen to vary slightly from one series to another in such a way that the lower constant is always obtained with the older sample. It should be added here that the constancy of the catalytic activity during a series of runs has often been controlled by repetition of selected runs, and in some cases it was found to be necessary to discard a number of runs due to an important drop in activity. The runs given in the tables are listed in chronological order within each series (table). The tables, however, are not placed in chronological order.

In connection with the ageing of the catalyst it should also be mentioned that a catalyst which has been aged at a higher temperature has a much

Table 8. 380°C. Variation of $(\text{CO}_2)_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.0290 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.20}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.438	24.60	49.20	0.17	0.93	25.10	4.13	4.1	0.0288
2	2.471	23.60	27.50	0.18	24.12	24.60	5.81	5.8	0.0290
3	2.367	24.00	12.70	0.22	37.88	25.20	9.45	11.0	0.0342
4	2.404	22.90	5.50	0.14	45.96	25.50	13.96	15.6	0.0332
5	2.363	24.70	5.11	0.19	44.10	25.90	14.45	14.0	0.0279
6	2.358	23.30	3.09	0.21	47.10	26.30	17.31	16.9	0.0281
7	2.308	24.20	35.80	0.23	12.87	26.90	5.38	4.6	0.0246
8	2.304	23.90	0	0.18	49.92	26.00	24.5	24.0	0.0279
Average									0.0292

Table 9. 380°C. Variation of space velocity (and $(\text{CO})_0$ and $(\text{H}_2\text{O})_0$). Amount of catalyst3.00 g. Rate equation for forward reaction: $r_f = 0.0352 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.20}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	4.629	25.90	0	0.19	23.01	50.90	19.6	18.1	0.0304
2	0.781	13.10	0	0.10	10.00	76.80	61.5	63.6	0.0380
3	0.400	11.90	0	0.09	9.91	78.10	79.3	79.7	0.0357
4	1.667	12.10	0	0.09	12.81	75.00	45.1	45.0	0.0350
5	2.367	12.20	0	0.09	12.51	75.20	37.9	37.2	0.0339
6	3.100	12.30	0	0.09	13.31	74.30	32.9	31.8	0.0329
7	3.863	12.40	0	0.09	12.71	74.80	29.3	26.9	0.0298
8	1.750	31.00	0	0.23	34.57	34.20	29.4	32.4	0.0410
9	3.471	33.20	0	0.25	31.95	34.60	20.0	20.8	0.0376
10	5.192	34.30	0	0.26	32.24	33.20	15.7	16.3	0.0372
11	0.467	28.90	0	0.22	37.88	33.00	55.1	55.0	0.0350
12	2.325	36.50	0	0.27	37.83	25.40	23.0	23.1	0.0354
Average									0.0352

lower activity when subsequently being used at a lower temperature than a catalyst which has been aged at this temperature. For instance if a catalyst sample has been aged at 500°C for two weeks its rate constant at 380°C will be less than $\frac{1}{2}$ of that of a sample having been aged for the same period at 380°C. This phenomenon also contributes to the result that it has been possible to avoid diffusion restriction at relatively high temperatures.

It appears from the tables that a wider variation of partial pressures has been applied for the runs at temperatures of 380°C and below than at higher

Table 10. 400°C. Variation of space velocity (and $(\text{CO})_0$ and $(\text{H}_2\text{O})_0$). Amount of catalyst3.00 g. Rate equation for forward reaction: $r_f = 0.054 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.20}}{(\text{CO}_2)^{0.65}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.358	35.50	0	0.27	37.43	26.80	29.0	30.2	0.058
2	1.200	34.80	0	0.26	38.84	26.10	40.1	41.7	0.058
3	0.613	35.80	0	0.27	38.73	25.20	51.3	51.3	0.054
4	1.213	34.90	0	0.26	38.34	26.50	39.9	42.2	0.062
5	4.696	37.60	0	0.28	36.62	25.50	19.6	19.6	0.054
6	1.225	23.90	0	0.18	25.02	50.90	49.2	54.0	0.065
7	2.267	23.00	0	0.17	24.03	52.80	37.4	39.0	0.058
8	0.613	22.60	0	0.17	25.53	51.70	66.1	69.0	0.060
9	0.317	26.00	0	0.20	23.80	50.00	77.9	79.6	0.058
10	3.604	24.80	0	0.19	25.61	49.40	28.6	29.0	0.055
Average									0.058

Table 11. 420°C. Variation of (CO)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction $r_f = 0.128 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant <i>k</i>
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.400	25.90	0	0.19	23.71	50.20	47.9	47.5	0.124
2	2.363	11.80	0	0.09	36.11	52.00	60.4	63.3	0.140
3	2.467	38.10	0	0.29	11.71	49.90	41.8	42.3	0.130
4	2.283	5.85	0	0.04	41.51	52.60	73.1	74.6	0.134
5	2.317	48.10	0	0.36	0.64	50.90	40.0	40.9	0.132
6	2.400	24.40	0	0.18	22.72	52.70	49.1	45.4	0.108
Average									0.128

Table 12. 420°C. Variation of (H₂O)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.105 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant <i>k</i>
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.400	24.40	0	0.18	22.72	52.70	45.1	45.4	0.107
2	2.317	24.00	0	0.18	0.42	75.40	48.4	48.2	0.104
3	2.496	23.90	0	0.18	10.02	66.90	45.9	45.2	0.102
4	2.413	24.40	0	0.18	34.02	41.40	43.4	42.9	0.103
5	2.421	23.70	0	0.18	47.42	28.70	41.3	40.9	0.103
Average									0.104

Table 13. 420°C. Variation of (CO₂)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.098 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant <i>k</i>
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.463	22.30	28.90	0.17	24.13	24.50	15.2	15.7	0.102
2	2.342	23.80	37.90	0.18	12.32	25.80	14.0	14.2	0.100
3	2.308	24.70	13.70	0.19	35.81	25.60	22.4	22.8	0.100
4	2.375	23.00	50.50	0.17	1.43	24.90	11.8	11.6	0.096
5	2.267	24.30	6.10	0.18	42.92	26.50	29.7	30.0	0.100
6	2.258	24.40	41.50	0.18	7.52	26.40	13.8	13.0	0.092
7	2.242	24.60	0	0.18	49.12	26.10	40.2	35.1	0.073
Average									0.095

Table 14. 420°C. Variation of space velocity. Amount of catalyst 3.00 g. Rate equation for forward reaction $r_f = 0.080 \cdot \frac{(\text{CO}) \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	1.346	19.80	0	0.15	42.05	38.00	52.5	57.1	0.096
2	0.629	18.80	0	0.14	45.76	35.30	70.3	71.8	0.086
3	2.533	22.80	0	0.17	44.13	32.90	36.6	37.6	0.084
4	4.304	22.60	0	0.17	46.63	30.60	27.6	28.5	0.085
5	1.371	15.50	0	0.13	33.27	51.10	58.1	59.3	0.084
6	5.446	22.20	0	0.17	41.93	35.70	25.0	24.4	0.077
Average									0.085

Table 15. 460°C. Variation of (CO)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.104 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.30}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.279	25.20	25.40	0.07	23.73	25.60	21.7	22.8	0.110
2	2.321	12.70	24.20	0.04	36.26	26.80	25.9	25.9	0.104
3	2.250	30.60	24.80	0.10	18.60	25.90	21.1	21.7	0.108
4	2.325	19.50	24.70	0.07	28.33	27.40	23.4	23.7	0.106
5	2.304	6.18	24.10	0.02	41.50	28.20	30.6	28.6	0.096
6	2.254	36.80	24.40	0.13	11.47	27.20	20.5	19.7	0.099
7	2.308	24.60	24.10	24.10	0.10	27.10	19.0	17.6	0.092
8	2.333	24.10	25.30	0.07	23.53	27.00	21.9	21.4	0.101
9	2.288	9.13	25.00	0.02	38.35	27.50	27.8	27.6	0.103
10	2.275	37.90	24.90	0.12	9.98	27.10	20.0	19.7	0.102
Average									0.102

In run No. 7 the feed gas contains an essential amount of H₂.

Table 16. 460°C. Variation of (H₂O)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.112 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.30}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.483	23.70	27.50	0.06	22.54	26.20	21.2	21.0	0.111
2	2.463	23.20	27.10	0.05	11.25	38.40	24.1	24.4	0.114
3	2.496	23.80	27.10	0.08	0.12	48.90	25.3	25.5	0.113
4	2.475	23.10	28.30	0.08	16.02	32.50	22.4	21.8	0.108
5	2.450	23.50	29.40	0.06	4.84	42.20	23.9	24.2	0.114
6	2.421	23.60	30.30	0.07	27.63	18.40	18.5	18.7	0.114
7	2.279	25.20	25.40	0.07	23.73	25.60	23.0	22.8	0.111
Average									0.112

Table 17. 460°C. Variation of $(\text{CO}_2)_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.140 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.80}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.392	23.30	29.10	0.05	24.05	23.50	24.6	26.7	0.155
2	2.313	24.50	36.40	0.07	12.53	26.50	23.4	23.9	0.144
3	2.325	24.20	12.10	0.07	36.53	27.10	36.0	35.9	0.140
4	2.346	22.90	48.80	0.07	1.73	26.50	20.4	20.8	0.143
5	2.342	24.60	18.30	0.07	29.13	27.90	31.3	30.1	0.133
6	2.321	23.30	31.00	0.06	18.84	26.80	25.5	25.5	0.140
Average									0.142

temperatures. This is due to two reasons. Firstly, at temperatures above 380°C the catalyst is quite easily reduced to elementary iron which catalyzes the decomposition of CO to C and CO₂, if the water partial pressure is reduced below a certain limit; this limit is not exactly known, it can, however, be mentioned that at 420°C this reduction does take place, if the water partial pressure is half that of the CO partial pressure. Secondly, as mentioned above, it was necessary to superimpose a constant CO₂-partial pressure at all runs performed at 460°C and 500°C. For this reason the results obtained at the higher temperatures may be less certain than those obtained at 380°C and below.

The tables containing data obtained at varying space velocities show that the rate formulas are valid over a quite large range of conversion. The fact that good agreement is obtained also at high conversions shows that the

Table 18. 500°C. Variation of $(\text{CO})_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.244 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.35}}{(\text{CO}_2)^{0.50}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.133	12.10	24.80	0.03	31.77	31.30	45.9	47.6	0.258
2	2.163	5.01	25.60	0.02	39.27	30.10	52.0	52.0	0.244
3	2.183	26.30	23.50	0.08	19.42	30.70	38.1	38.7	0.251
4	2.358	29.50	24.00	0.09	10.51	35.90	36.9	35.9	0.234
5	2.558	16.00	22.80	0.06	29.34	31.80	39.7	39.9	0.246
6	2.292	17.50	23.80	0.06	25.34	33.30	41.8	40.0	0.228
7	2.304	8.57	23.60	0.02	34.01	33.80	48.6	49.7	0.252
8	2.404	23.00	23.70	21.60	0.20	31.50	30.2	28.5	0.222
9	2.288	35.20	25.10	0.11	6.59	33.00	34.3	32.8	0.227
Average									0.240

In run No. 8 the feed gas contains an essential amount of H₂.

Table 19. 500°C. Variation of $(\text{H}_2\text{O})_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.272 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.35}}{(\text{CO}_2)^{0.50}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.238	25.90	21.60	0.07	12.43	40.00	45.0	43.1	0.253
2	2.325	23.70	22.20	0.08	2.22	51.80	48.4	50.8	0.293
3	2.300	25.00	22.10	0.09	23.81	29.00	39.8	39.1	0.264
4	2.267	25.60	22.20	0.08	6.02	46.10	46.5	45.5	0.263
5	2.242	25.50	22.50	0.08	0.00	52.00	48.4	48.0	0.268
6	2.183	26.30	23.50	0.08	19.42	30.70	40.6	38.7	0.251
7	2.233	25.20	23.10	0.07	30.53	21.10	35.4	34.5	0.260
Average									0.265

assumption concerning the stoichiometric number being equal to 1 is not contradicted by the experiments.

The values of the exponents l , m , and n , obtained at the different temperatures, are summarized in Table 21.

The value shown of l at 360°C has been obtained only from the graphic representation. The values shown at 400°C are those obtained at 380°C, and which have been applied for a series of runs of varying space velocity (Table 10).

It appears that the variation of l , m , and n over the whole temperature range is small, in most cases within the experimental uncertainty. It is perhaps surprising that the value of l both at low and high temperatures falls below 1. In this connection it should be mentioned that the runs at 330°C with varying $(\text{CO})_0$ have been repeated three times with identical results. There is some indication that the value of m increases, whereas n decreases numerically when the temperature rises above 420°C; it must, however, be borne in mind that the values obtained at 460° and 500°C are less certain than those obtained at lower temperatures.

Table 20. 500°C. Variation of $(\text{CO}_2)_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction: $r_f = 0.300 \cdot \frac{(\text{CO})^{0.80} \cdot (\text{H}_2\text{O})^{0.35}}{(\text{CO}_2)^{0.50}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. calc. %	Conv. exptl. %	Rate constant k
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.967	21.10	40.60	0.06	17.64	20.60	26.8	28.5	0.326
2	2.254	27.10	22.20	0.08	23.52	27.10	40.6	40.0	0.292
3	2.358	25.80	48.90	0.07	0.00	26.00	30.4	31.6	0.318
4	2.279	24.90	35.60	0.07	12.93	26.50	35.4	36.2	0.311
5	2.192	24.90	22.40	0.07	25.83	26.80	41.9	42.6	0.309
6	2.304	24.10	12.80	0.07	37.13	25.90	46.6	46.7	0.301
7	2.300	24.60	29.90	0.07	19.33	26.10	37.2	35.5	0.278
Average									0.302

Table 21.

Temperature	<i>l</i>	<i>m</i>	<i>n</i>
330°C	0.80	0.25	-0.65
360°C	(1.00)	—	—
380°C	1.00	0.20	-0.65
400°C	(1.00)	(0.20)	(-0.65)
420°C	1.00	0.25	-0.60
460°C	0.80	0.30	-0.60
500°C	0.80	0.35	-0.50

As the variation of *l*, *m*, and *n* is small it is possible to establish a single rate expression which is valid with fairly good accuracy over the whole temperature range 330°—500°C. Such an expression would be

$$r_f = k(T) \cdot \frac{(\text{CO})^{0.90} \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.60}} \quad (11)$$

where *k*(*T*) varies with the temperature.

This expression is in essential agreement with the preliminary results reported by Stelling and Krusenstierna⁵, but differs strongly from that proposed by Kul'kova and Temkin¹. It differs more or less strongly from the other rate equations proposed.

Due to the dependence of the ageing effect upon the ageing temperature (and time) the data given in Tables 2—20 cannot be used for calculation of the apparent activation energy. For this reason a special series of runs at different temperatures was made with a catalyst which had been aged at 500°C. For the runs at 500°C and 460°C a CO₂-containing feed gas was used; for the runs at 380, 360 and 330°C a feed gas without CO₂ was used; at 420° runs with both kinds of feed gas have been used. The respective values of *k* were calculated according to the previously applied method using the "average" rate expression (eqn. 11) for the forward reaction (Table 22). By plotting ln *k* against 1/*T* a straight line is obtained (Fig. 6). This fact further

Table 22. Variation of reaction temperature. Amount of catalyst 3.00 g. Catalyst stabilized at 500°C. Rate equation for forward reaction $r_f = k \cdot \frac{(\text{CO})^{0.90} \cdot (\text{H}_2\text{O})^{0.25}}{(\text{CO}_2)^{0.60}}$

No.	Total feed mole/h	Feed gas composition, %					Conv. exptl. %	Rate constant <i>k</i>	Reaction temperature °C
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.367	25.00	23.40	0.07	1.43	50.10	54.9	0.36	500
2	2.342	24.90	23.60	0.07	0.13	51.30	31.6	0.144	460
3	2.350	24.60	23.90	0.07	0.23	51.20	12.9	0.049	420
4	2.400	24.30	0	0.07	24.43	51.20	30.8	0.042	420
5	2.388	24.30	0	0.07	24.73	50.90	16.2	0.0134	380
6	2.379	24.00	0	0.07	24.63	51.30	11.2	0.0070	360
7	2.375	23.90	0	0.07	24.23	51.80	5.85	0.0024	330
8	2.371	23.50	24.30	0.07	1.43	50.70	54.3	0.35	500

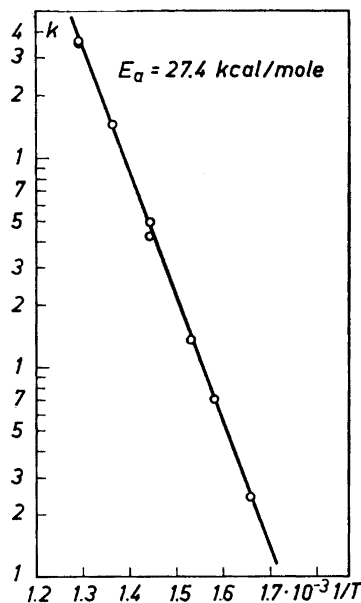


Fig. 6. $\log k$ vs. reciprocal absolute temperature. The "average" rate expression (eqn. 11) has been applied for the calculations.

confirms that diffusion restriction has not influenced the experimental results. From the slope of the straight line an apparent activation energy of 27.4 kcal per mole is calculated.

As often stated in the literature^{5,9,10} it is necessary to apply the outmost caution when trying to deduce a mechanism from a rate expression as different mechanisms may very well yield rate expressions which are approximations of each other. Without going much into detail a reasonable mechanism for the above rate expression may seem to be the following: The rate determining step is reaction between gaseous CO and oxidized surface sites, or perhaps chemisorption of CO. CO₂ and H₂O are strongly adsorbed on the surface, whereas H₂ is not adsorbed.

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REFERENCES

1. Kul'kova, N. V. and Temkin, M. I. *Zhur. Fiz. Khim.* **23** (1949) 695.
2. Atwood, K., Arnold, M. R. and Appel, E. G. *Ind. Eng. Chem.* **43** (1950) 1600.
3. Kodama, S., Fukui, K., Tame, T. and Kinoshita, M. *Catalyst (Japan)* **8** (1952) 50.
4. Kodama, S., Mazume, A., Fukuba, K. and Fukui, K. *Bull. Chem. Soc. Japan* **28** (1955) 318.
5. Stelling, O. and Krusenstierna, O. v. *Acta Chem. Scand.* **12** (1958) 1095.
6. Atroshchenko, V. J. and Bibr, B. *Zhur. Priklad. Khim.* **32** (1959) 997; *Chem. Abstr.* **53** (1959) 15735.

7. Kirillov, I. P. *Trudy Ivanovsk. Khim. — Teknol. Inst.* **1956** No. 5, p. 45; *Chem. Abstr.* **53** (1959) 11969.
8. Lebedev, A. T. and Popov, B. I. *Trudy Ivanovsk. Khim. — Teknol. Inst.* **1958** No. 7, p. 53; *Chem. Abstr.* **54** (1960) 8251.
9. Weller, S. *A. I. Ch. E. Journal* **2** (1956) 59.
10. Boudart, M. *A. I. Ch. E. Journal* **2** (1956) 62.
11. Hougen, O. A. and Watson, K. M. *Chemical Process Principles*, John Wiley & Sons, New York 1947, Part III, Chapter XX.
12. Hoogschagen, J. *Ind. Eng. Chem.* **47** (1955) 906.

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