Design of Experiments on the Kinetics of the Water-Gas Shift Reaction

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Experiments on the continuous catalytic water-gas shift reaction have been carried out making full use of the principles of statistical design to elucidate the reaction mechanism. Instantaneous reaction rates were determined for sixteen different combinations of the five variables: partial pressures of carbon monoxide, hydrogen, carbon dioxide, and temperature. Nitrogen gas was used as an inert diluent to make up the total pressure to 1 atm. From the analysis of variance of these sixteen runs it can be shown that the Temkin mechanism for the water-gas shift reaction cannot represent the data within the experimental accuracy. A tentative alternative mechanism which is consistent with the data obtained is presented. The work shows that while it is possible to obtain useful empirical kinetic data from small, well-planned experiments, both highly precise experimental data and very careful statistical treatment are required. When these are available, a very marked reduction in the amount of experimental work can be effected.

The water-gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$ has been extensively studied and widely used for many years in the preparation of synthesis gas. Though most catalysts in commercial use are of a similar nature, engineering reactor design requires detailed evaluation of the kinetics for specific catalysts. The study presented here was undertaken to provide a basic background to the empirical catalyst tests with the hope of shedding some light on the mechanism of the reaction as well as some quantitative rate data.

The catalyst chosen was typical of commercial promoted iron oxide catalysts and was used as cylindrical pellets ⅜ in. by ⅜ in. diameter. To avoid excessive influence of nonuniform catalyst packing a reactor diameter of 2 in. was chosen and the bed depth adjusted so that the effect of residence time on conversion was independent of bed depth. Figure 1 shows the result of varying bed depth and gas velocity in constant proportion to maintain a fixed nominal residence time. These data serve to demonstrate independence of conversion on mass transfer in the gas phase between pellets as well as the substantial freedom from channelling of the gas through the bed.

The reactor was operated in a continuous three-shift program in which operating variables were maintained at set levels until the output quantities became steady. A continuous complete material balance was maintained as a check against analytical errors and unsuspected operating upsets.

EXPERIMENTAL DESIGN

It seemed highly desirable to obtain differential rates for kinetic analysis. The mechanical and mass transfer considerations however dictated a reactor which gave finite conversions. Furthermore it was highly desirable to avoid operating under conditions at which the reverse reaction rate is appreciable. These circumstances led us to determine the change in space velocity required to accomplish a change of conversion from 20% to 30% for a variety of inlet gas compositions. In this range equilibrium calculations showed the reverse reaction rate to be less than 5% of the forward rate, with the exception of one run in which the reverse rate may have been 13%. The two conversion points experimentally determined lay in all cases on a straight line through the origin of a plot of conversion vs. residence time (Figure 2). The slope of this line could therefore be used as a measure of the differential rate.

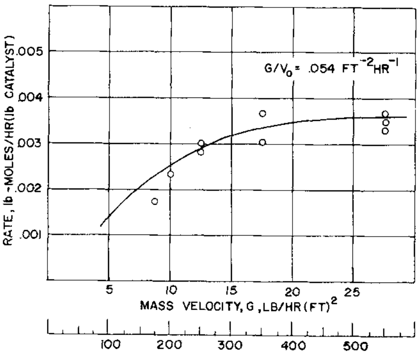

Fig. 1. Effect of mass velocity on reaction rate.

In practice numercial rather than graphical methods were used and the differential rates determined from the formula

$$R = \frac{(p_{CO})_{20} - (p_{CO})_{30}}{t_{20} - t_{30}}$$

The rate thus computed was taken to be the instantaneous rate for a gas composition calculated for 25% conversion of the feed carbon monoxide. The residence time to achieve this conversion falls approximately midway between t_{20} and t_{30}.

The factors chosen in the experimental design were the partial pressures of the four components of the gas mixture and the temperature. Diluent nitrogen was added to maintain a total pressure of 1 atm. in all cases.

In previous work of Temkin (9) and associates evidence was presented for a kinetic expression of the form

$$R = -\frac{dp_{CO}}{dt} = k\, p_{CO} \left(\frac{p_{H_2O}}{p_{H_2}}\right)^{1/2} \qquad (1)$$

Generalizing this slightly and taking logarithms one finds

$$\log R = \log Z - \frac{E}{RT} + b_2 \log p_{CO} + b_3 \log p_{H_2O} + b_4 \log p_{H_2} + b_5 \log p_{CO_2} \qquad (2)$$

Experimental conditions were chosen to test the validity of Equation (2) and at the same time to evaluate the param-

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Table 1. Experimental Design

Conditions					−Log R (Observed)	Conditions					−Log R (Observed)
X_1	X_2	X_3	X_4	X_5		X_1	X_2	X_3	X_4	X_5	
+1	−1	−1	−1	−1	2.0119, 2.0540	−1	−1	−1	−1	+1	2.5406
−1	+1	−1	−1	−1	2.3575	+1	+1	−1	−1	+1	1.8745
−1	−1	+1	−1	−1	2.6021	+1	−1	+1	−1	+1	1.6021
+1	+1	+1	−1	−1	1.8239	−1	+1	+1	−1	+1	2.4901
−1	−1	−1	+1	−1	2.1733, 2.1200	+1	−1	−1	+1	+1	1.7040
+1	+1	−1	+1	−1	1.9412	−1	+1	−1	+1	+1	2.5302
+1	−1	+1	+1	−1	2.0301	−1	−1	+1	+1	+1	2.5023
−1	+1	+1	+1	−1	2.5107	+1	+1	+1	+1	+1	1.6108

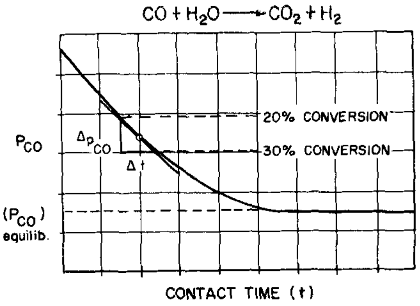

Fig. 2. Schematic determination of differential reaction rate.

eters Z, E/R, b_2, b_3, b_4, and b_5. Since there were five factors in Equation (2), a half replicate of a 2^5 factorial design suggested itself. The authors' experimental techniques were well established by prior work, and it was expected that R could be determined within about 10%. From the proposed sixteen runs the absence of interactions between the five factors was to be tested. If these were indeed negligible, then Equation (2) was validated and estimates of the parameters could be made.

EQUIPMENT AND OPERATING PROCEDURES

The gases used were commercially pure grade carbon monoxide (purity 96.8%); carbon dioxide (liquid, bone dry, 99.8%); hydrogen, water pumped (purity 99.7%); nitrogen, water pumped (purity 99.7%); methane, technical grade (minimum purity 96%, ethane, propane, nitrogen, and trace oxygen gas impurities).

The cylinders containing the various gases were connected to a manifold feeding into rotameters. Each gas was metered separately. With a tri-flat type of rotameter, the flow was steady, and the accuracy of metering was within 1% of the scale reading. The gases were metered at a pressure of 50 lb./sq. in gauge to achieve steadiness of the float operation. The metered gases were next led into a jet mixer in which the gases were mixed. The jet mixer was so designed that the component with the largest volume swept off the smaller-volume component by flowing over the jets of the individual streams, as shown in Figure 3. The gas from the jet mixture next flowed into a packed tower containing 1/16-in. diameter stainless steel balls. This tower served to mix the dry gases thoroughly before they were fed to the reactor unit. With such a dynamic mixing system the errors in batch mixing of gases in tanks could be minimized. In a batch-mixing procedure in which a large tank was filled with the components successively, with a sensitive pressure gauge used as an indicator of the amount of gas to be charged, the carbon monoxide content could not be controlled to better than ±2% at the level of 10% carbon monoxide Since, in the kinetic runs, the net change in carbon monoxide content from feed to exit would be not more than 2%, it was necessary to devise the flow method which allowed the control of feed-gas composition to better than ±0.2% of carbon monoxide.

Steam was added to the premixed dry gases before they entered the reactor unit. It was generated in a boiler consisting of stainless steel packed piping in the configuration of an H. The pipe was packed with stainless steel mesh packing and heated externally by a burner. Distilled water to the boiler was metered through a tri-flat rotameter which could control the water rate to within 1% of the full-scale rating. The steam was superheated by electrically heated coils before mixing with the gas.

The hot mixture of steam and gas entered the reactor tube from the side inlet at the top. The reactor tube consisted of a Schedule 80 2-in. seamless steel pipe, 42¾ in. long, containing a mild-steel thermocouple well located axially in the tube. A side arm was located at the top of the reactor for the purpose of loading the catalyst into the reactors. The catalyst rested on a perforated metal plate which was welded to a support rod.

Temperature control in the reactor was obtained by electrical coils surrounding the reactor walls and divided into four sections, each controlled individually by a powerstat. Before the start-up an equivalent flow of nitrogen was maintained through the reactor at the temperature of the experiment, and the heaters were adjusted to obtain a thermal balance of the reactor in which enough heat was supplied to balance the radiation losses of the insulated reactor at flow conditions, as indicated by identical inlet and exit gas temperatures. The powerstat settings for various flow rates and temperatures were obtained initially. With such a technique the longitudinal temperature profile in the reactor could be maintained constant to within less than ±2°C. Since the kinetic runs were to be formed in the region of low conversion, no significant temperature rise of the bed due to the heat of reaction was expected. An error analysis showed that the variation in temperature contributed a major portion (60 to 70%) of the experimental error in the measurement of the carbon monoxide-conversion rate, but this variation was still small enough to warrant considering the reactor to be isothermal.

Table 2. Code

Symbol	Variable	Level −1	Level +1
X_1	1/T, (°K)$^{-1}$	$\frac{1}{583}$	$\frac{1}{613}$
X_2	log p_{CO}	0.04	0.08
X_3	log p_{H_2O}	0.20	0.40
X_4	log p_{CO_2}	0.07	0.18
X_5	log p_{H_2}	0.07	0.14

The exit gas from the reactor was cooled by means of a water-cooled, stainless steel condenser coil. The condensed steam was separated from the exit gas in a stainless steel separator containing a gauge glass. The exit gas from the separator passed through a wet-test meter and was then discarded.

Sample lines were provided both on the dry inlet feed-gas line and the exit-gas line leaving the separator. These sample lines were connected to a specially modified dry gas bulb, sealed by mercury through a three-way stopcock. The sample of the gas from this dry bulb could be analyzed in an Orsat apparatus. A continuous analysis was also performed both on inlet and exit gases for their carbon monoxide and carbon dioxide contents, with a specially modified gas analyzer. For greater accuracy the range of the analyzer was magnified by use of a 4 to 9% range (for carbon monoxide) instead of 0 to 9%. This was done by using 4% carbon monoxide in nitrogen as zero gas instead of nitrogen alone. A similar alteration in range also was used for carbon dioxide concentrations.

The statistical design predetermined the exit compositions; the inlet compositions were therefore also fixed because the reaction rate was to be measured at 25% conversion. Hence, one needed only to vary the space velocity or the contact time to achieve the two desired conversion levels of 20 and 30%. To achieve this with a fixed amount of catalyst a bleed valve was located just before the inlet to the reactor which regulated the amount of steam-gas mixture introduced over the catalyst. By suitable manipulation of this bleed valve the exit carbon monoxide analysis (as indicated by the continuous infrared instrument) was brought to the desired level set by the experimental design. With this novel technique one is able to achieve quick, reliable, and accurate kinetic data.

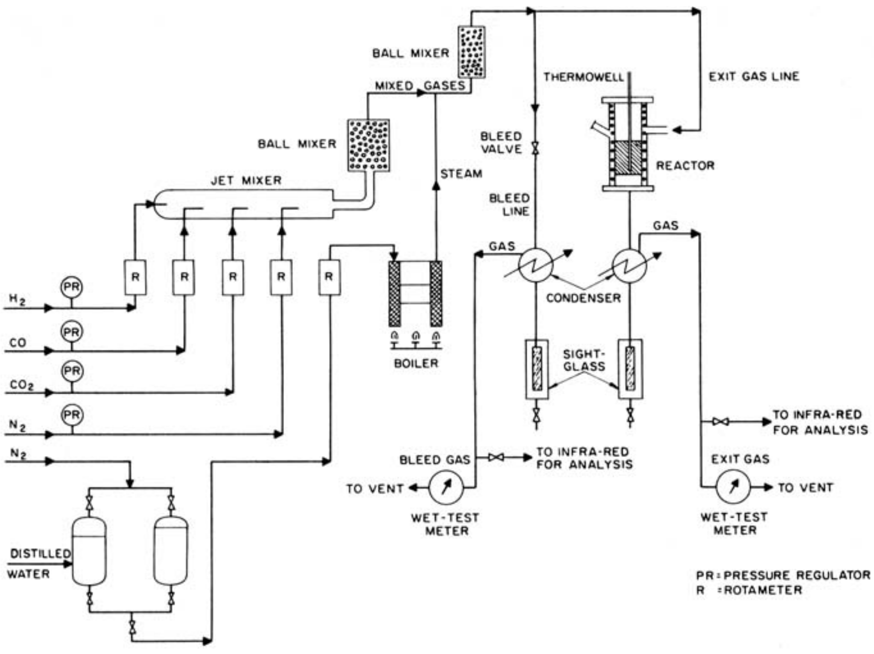

Fig. 3. Flow scheme of carbon monoxide converter unit.

The amount of gas vented through the bleed valve was measured by another wet-test meter. The exit-gas quantity as measured by the first wet-test meter gave the volume of gas (after correction for expansion) that passed over the catalyst and thus a measure of the contact time.

The catalyst used in this experiment was subjected to an accelerated aging process to eliminate the initial, variable, high activity of fresh catalyst. The aging process consisted of a high-temperature treatment with a gas containing 65% hydrogen, 35% carbon monoxide, to which steam was added in the ratio 10/1. Initially the catalyst was kept in contact with this mixture at 450°C. for 2 hr., followed by 16 hr. at 650°C.

In the runs reported here a single catalyst charge was used. It was typical of commercial catalyst, having a surface area of 5 to 6 sq.m./g. and pore volume of 0.25 to 0.30 ml./g. The normal sequence of operations consisted of continuous running at high space velocity to steady conversion, shift to low space velocity and run to steady conversion, followed by a return to the high space velocity as a check on the constancy of catalyst performance.

STATISTICAL ANALYSIS OF THE DATA

The experimental design in coded levels of the variables and the observed experimental rates are shown in Table 1. The code is explained in Table 2. It will be noted that two runs were replicated to corroborate the authors' estimate of the variance of a determination. This variance includes experimental errors as well as uncertainties in estimating the rate from the data.

The usual statistical analysis of two level factorial data consists of fitting a linear plus interaction model, that is an equation of the form of (3), by means of least squares. The unaccounted-for portion of the over-all variation is then used as a measure of error

$$\begin{aligned} Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 \\ + b_4X_4 + b_5X_5 \\ + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 \\ + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{25}X_2X_5 \\ + b_{34}X_3X_4 + b_{35}X_3X_5 \\ + b_{45}X_4X_5 \end{aligned} \tag{3}$$

to test the significance of the individual terms of the model.

Analysis of variance of these data shows strong effects only from T and T x p_{H_2} with weaker effects to be considered from p_{H_2}, p_{H_2} x p_{H_2O}, and T x p_{H_2O}. Figure 4 shows a half-normal plot of the sixteen regression coefficients for Equation (3) which is tabulated in Table 3. This plotting technique, due to Daniel (*3, 4*), is based on the fact that each sum of squares in Table 3 is the difference of two sums of eight data points each. If these data were purely random, the differences would be the range of random samples of two from a nearly normal population. The expected cumulative distribution (with sign ignored) would give a straight line as plotted in Figure 4. When the fifteen differences in Table 3 (exclusive of the mean) are arranged in increasing order of magnitude, the probability that a number be no larger than the greatest is 14.5/15. In general for n contrasts one assigns a probability

$$P_i = (i - 1/2)/n$$

to the i^{th} contrast in increasing order of size. The ordinate scale in Figure 4 is designed to produce a straight line when P_i is plotted against the size of contrast i, provided there are no real effects. One sees that only the largest effects exceed the magnitude to be expected from a purely random distribution. It is again evident that only the effects of p_{H_2}, p_{H_2O}, and T can be considered significant.

In particular the strong interactions with temperature suggest a different kinetic model with more than one temperature dependent rate constant. One can conclude that Equation (2) is not a satisfactory representation of the data.

The authors note that pooling all of the nonsignificant effects in Equation (3) leads to a residual mean square of 0.0077, to be compared with the replication error mean square of 0.0023 for the response, log R. Without more replications, one cannot conclude that this difference is significant.

In more familiar terms one finds that Equation (3), retaining only the terms in T, p_{H_2}, p_{H_2O}, and their interations, predicts the observed rates over the range of 0.0025 to 0.025 with an average standard error of ±0.0024. The higher rates are thus reasonably well predicted.

The interaction terms are not readily interpreted on the model of Equation (3). Since they are large and undoubtedly real, one is led to examine alternative mechanisms of reaction and the corresponding mathematical models.

TABLE 3. ANALYSIS OF VARIANCE, LOG R

Source	Sum of squares	Degrees of freedom	Source	Sum of squares	Degrees of freedom
Total	75.5169	16	log p_{CO_2}	0.0056	1
Mean	73.553	1	log p_{CO}	0.00004	1
$1/T$	1.6309*	1	$(1/T)$ log p_{CO_2}	0.0038	1
log p_{H_2}	0.0222*	1	$(1/T)$ log p_{CO}	0.0018	1
log p_{H_2O}	0.0001*	1	log p_{CO} log p_{CO_2}	0.0097	1
$(1/T)$ log p_{H_2}	0.1287*	1	log p_{CO} log p_{H_2O}	0.0206	1
$(1/T)$ log p_{H_2O}	0.0586*	1	log p_{CO} log p_{H_2}	0.0072	1
log p_{H_2} log p_{H_2O}	0.0537*	1	log p_{CO_2} log p_{H_2O}	0.0204	1
log p_{H_2} log p_{CO_2}	0.00002	1			

* Retention of these terms only gives a residual sum of squares of 0.0693 with nine degrees of freedom, or residual mean square = 0.0077. Error mean square based on 2 replicates = 0.0023.

TENTATIVE MECHANISM

The role of diffusion in the catalyst pores can be assessed by the methods of Weisz (*10*) by the use of an effective diffusivity, $D = 0.07$ sq. cm./sec. at 600°K, based on measurements (*2*) on a similar commercial catalyst. By these criteria pore diffusion should have only a negligible effect on the over-all rate of reaction. The authors have analyzed their data on the assumption that the measured rates are those of the surface reaction unmodified by mass transfer phenomena.

The authors' experiments have established the following experimental facts for which any mechanism must account:

1. The partial pressures of carbon monoxide and carbon dioxide have a negligible influence on the reaction rate.
2. The rate increases with the partial pressure of hydrogen, especially at the higher steam pressure.
3. The effects of gas composition changes are much less marked at low temperature than at high.

The observations are of course applicable only in the range of variables covered, that is at 20 to 30% conversion, atmospheric pressure, 310° to 350°C.

The promoting effect of hydrogen has not been reported in previous work, none of which however has dealt with the low conversions, relatively low temperature, and the wide range of feed gas compositions reported here (*8*).

Previous work (*7*) has suggested that the oxidation of carbon monoxide involves the ferric-ferrous iron equilibrium in the catalyst surface. A simple mechanism embodying this thought can be written as follows:

$$H_2O + MO \rightleftharpoons H_2O \cdot MO \qquad k_1, k_1' \qquad (4)$$

$$H_2O \cdot MO \rightleftharpoons H_2 \cdot MO_2 \qquad k_2, k_2' \qquad (5)$$

$$H_2 \cdot MO_2 \rightleftharpoons MO_2 + H_2 \qquad k_3, k_3' \qquad (6)$$

$$CO + X \rightleftharpoons CO \cdot X \qquad k_4, k_4' \qquad (7)$$

Here one assumes that hydrogen and water are adsorbed on different sites than is carbon monoxide. The equilibrium ratio of ferric to ferrous ions in the surface may then be shown to be (*5*)

$$\frac{[MO_2]}{[MO]} = K_o \frac{p_{H_2O}}{p_{H_2}} \qquad (8)$$

The total number of metal-ion sites of all types is given by

$$L_M = [MO] \left\{ 1 + K_o \frac{p_{H_2O}}{p_{H_2}} + K(1 + K_2) p_{H_2O} \right\} \qquad (9)$$

where

$$K_o = K_1 K_2 K_3$$

$$K_1 = k_1/k_1', \text{ etc.}$$

If one supposes the sites capable of adsorbing carbon monoxide to be nearly all covered, one accounts for the lack of influence of the partial pressure of carbon monoxide. One must suppose the adsorbed carbon monoxide to react with one of the species involving hydrogen or water in the slow step of the reaction. If we suppose this to be $H_2O \cdot MO$

$$R = \frac{k_5 K_1 L_M \, p_{H_2O}}{1 + K_o \dfrac{p_{H_2O}}{p_{H_2}} + K_1 (1 + K_2) p_{H_2O}} \qquad (10)$$

or

$$\frac{1}{R} = \frac{1}{k_5 K_1 L_M} \cdot \frac{1}{p_{H_2O}} + \frac{K_2 K_3}{k_5 L_M} \frac{1}{p_{H_2}} + \frac{1 + K_2}{k_5 L_M} \qquad (11)$$

This form accounts qualitatively for most of the empirical conclusions but does not predict an influence of the steam pressure on the magnitude of the hydrogen effect.

A least-squares fit of the high-temperature data to Equation (11) results in

$$\frac{1}{R} = -10.64 + (6.09/p_{H_2O}) + (5.515/p_{H_2}) \qquad (12)$$

A negative constant has of course no physical justification. However an estimate of the 95% confidence region about the intercept of Equation (11) shows that the constant term is in fact -10.64 ± 64.6. Thus one cannot conclude from these data that the true value is in fact negative.

If one now fits Equation (11) under the restriction that all coefficients be positive, it is easily seen that the best fit will be obtained by choosing the intercept to be zero. The model can now be written

$$\frac{1}{R} = \frac{(4.746)}{p_{H_2O}} + (5.044)(1/p_{H_2}) \qquad (13)$$

Table 4 shows the standard error of prediction of the rate at the high temperature for each of the three predictors, Equations (3), (12), and (13). Evidently each is as good a predictor as any other. However since Equation (13) has a theoretical interpretation and involves only two parameters, it is to be preferred. Solving for R one finds

$$R = \frac{0.2107 \, p_{H_2O}}{1 + 1.063 \dfrac{p_{H_2O}}{p_{H_2}}} \qquad (14)$$

The predictions of Equation (14) are compared with observations in Figure 5. The low-temperature data are also reasonably well represented by this form, with a new set of constants, although the relative error is too large to lend any confidence to the precision of the constants.

Comparison of Table 4 with Figure 5 will emphasize that the standard error is a much more stringent test of fit than the usual casual comparison of observed and predicted values.

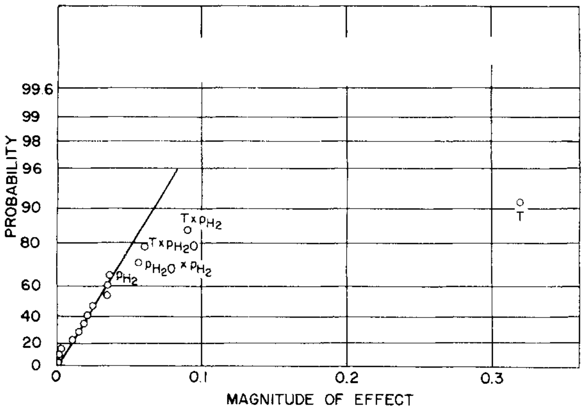

Fig. 4. Half-normal plot of coefficients for 16-point logarithmic model.

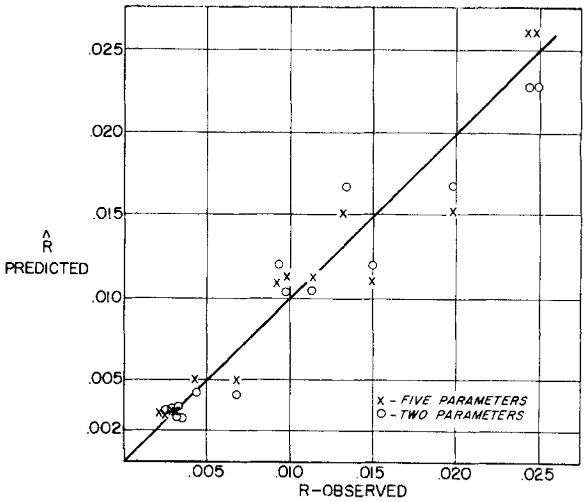

Fig. 5. Comparison of predicted and calculated rates.

TABLE 4. STANDING ERRORS OF PREDICTION

Variate predicted	Predictor	Parameters	Standard error	Degrees of freedom
R	Equation (3)	6	0.00239	9
R	Equation (13)	2	0.00338	6
R	Replicates	—	0.000628	2
$1/R$	Equation (12)	3	16.30	5
$1/R$	Equation (13)	2	15.16	5
$1/R$	Replicates	—	10.07	2

The relatively poor precision of the prediction of the rates at low temperatures is the result of least-squares fitting of $1/R$, in which experimental errors are magnified for small R. This distortion of the precision of a predictor is frequently encountered when the percentage error in the response is expected to be uniform over the range of experimentation. One then finds a more uniform variance if the response $1/R$ or $\log R$ is analyzed, and tests of significance can be made more reliably. However the resulting regression, when inverted to give a predictor for R, will have far from uniform confidence limits. No statistical treatment of the data appears to be available which will obviate this difficulty. As methods develop for direct least-squares fitting of nonlinear forms (*2a*) one may expect to obtain predictors with more uniform variance.

DISCUSSION

It is tempting to interpret the values in Equation (13) in terms of the rate constants and equilibrium constants of the mechanism leading to Equation (11). However this must be done with great caution. To avoid treating a nonlinear form the authors have considered only the eight high-temperature runs. There are thus only five degrees of freedom for error, too few to establish very narrow confidence limits on the coefficients. One must expect to find a fairly wide range of nearly compensating values for the parameters, all of which furnish equally good empirical predictors. Obviously one must be extremely cautious in deducing mechanisms from data such as these

When one takes Equation (14) at face value, the authors' data are consistent with a mechanism in which hydrogen and steam influence the rate only by their control of the ratio of ferrous to ferric surface ions. If hydrogen or steam is adsorbed, it is not in quantities sufficient to block the adsorption of carbon monoxide to a significant degree.

The present data do not give reliable temperature coefficients for the constants in Equation (14). One cannot say therefore whether or not the same equation will be adequate at the higher temperatures of commercial interest. It is entirely conceivable that the relative magnitudes of the adsorption terms will shift significantly with temperature, necessitating a different form at higher temperatures.

Neither can one be sure that Equation (14) holds for rates very close to equilibrium. However since the authors' gas feed compositions in general cover the range which would be covered by the exit gas if equilibrium were reached, it seems unlikely that a major departure from Equation (14) would be found. This implies that to satisfy equilibrium the reverse reaction must have the rate

$$R' = \frac{k'_o\, p^{\alpha}_{H_2}\, p^{\alpha}_{CO_2}}{p^{\alpha}_{CO}\, p^{\alpha-1}_{H_2O}\left[1 + K_o \dfrac{p_{H_2O}}{p_{H_2}}\right]} \qquad (15)$$

where α is undetermined (*6*). The mechanistic interpretation of Equation (15) is not very straightforward however. Further work would be required to verify its validity.

Thus while it appears possible to obtain useful empirical kinetic data from small well-planned experiments, both highly precise experimental data and very careful statistical treatment are required. Most alternative theoretical mechanisms which are qualitatively acceptable are not distinguishable by goodness-of-fit criteria, even with data of excellent precision by usual standards. Special experiments will have to be devised to test and distinguish between proposed mechanisms on points at which crucial differences are to be expected. Nevertheless in the present case one can reject the Temkin model for the range of variables studied here. A reasonably simple alternative can be proposed which is consistent both with the data and with a reasonable mechanism. While certainly not unique it gives a predictor which should be useful for many purposes.

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NOTATION

k_1, k_2, etc. = specific reaction rate

K_1, K_2, etc. = equilibrium constants

L_M = total surface concentration of adsorption sites, covered and bare, [moles (cu. ft. reactor)$^{-1}$]

$(p_{CO})_{20}$ = partial pressure of carbon monoxide in exit gas for contact time $+_{20}$ at which 20% of the feed carbon monoxide was converted

p_x = partial pressure of component x

R = differential reaction rate [moles sec.$^{-1}$ (cu. ft. reactor)$^{-1}$]

$[x]$ = surface concentration of x per unit volume of reactor [moles (cu. ft. reactor)$^{-1}$]

t = residence time

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