side of a question, just to clarify his ideas. If a research student could talk him out of a proposed experiment he was happy—"Look at all the work we've saved." A frequent discusser at meetings, he sometimes irritated people by comments that seemed impatient and blunt. But scientific argument was impersonal to him; the polite compliments as a preamble to the stroke of the knife were not his way.

It seemed at times as if Bancroft had little use for the mathematical approach to physical chemistry; he believed strongly in qualitative experimentation to answer clearly formulated questions, with quantitative work as confirmation of the theory thus propounded. Never did he let his men get lost in numbers without a definite idea of where the data were leading them. If an experiment didn't sustain his theory, he was the first to recognize that it was misleading or inapplicable, and to suggest another one that should settle the question.

Bancroft was serenely independent of campus politics; for many years he turned back his salary to buy equipment. He was never ruffled, harbored no grudges, and kept his social and professional lives separate. He played football at Harvard, followed sports ardently, and golfed and skated long after most people would have abandoned such exercise. He was greatly concerned, after an accident that gave him a serious concussion, lest his brain had been damaged, because his bridge game was for a time not up to its usual high quality.

His students fondly spoke of him as "Banty," yet he never called them by their first names, or palled around with them on parties. He dispensed no guidance, although somehow he managed to find fellowship support for a good man who was having hard sledding. Without making any conscious gesture, he inspired affection as well as admiration, and maintained scientific democracy because he never held his personal ideas as inherently superior or infallible. In contrast to self-seeking "promoters" of Research, jealous of priority, eager for subsidy irrespective of appropriate competence, he was a "gentleman-scholar" in the old-fashioned individual and collective meaning of these terms.

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[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

Kinetics and Mechanisms of the Two Opposing Reactions of the Equilibrium $CO + H_2O = CO_2 + H_2$[1]

BY WENDELL M. GRAVEN AND F. JOHN LONG

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A kinetic study has been made of the two opposing reactions which comprise the "water–gas equilibrium," equation 1. Experimental measurements were made using a quartz vessel at 900° and a flow rate which allowed a reaction time of approximately 0.5 second.

The results may be summarized in the rate expressions

$$\frac{d[H_2O]}{dt} = \frac{9.5 \times 10^{10} \exp(-57000/RT)[H_2]^{1/2}[CO_2]}{1 + 3.6 \times 10^{3}[CO]} \qquad \frac{d[CO_2]}{dt} = \frac{5.0 \times 10^{12} \exp(-67300/RT)[CO]^{1/2}[H_2O]}{(1 + 1.2 \times 10^{4}[H_2])^{1/2}}$$

which apply to the carbon dioxide–hydrogen and carbon monoxide–steam reactions, respectively.

Homogeneous chain mechanisms, involving the chain propagating steps $OH + CO \rightleftarrows H + CO_2$ and $H + H_2O \rightleftarrows OH + H_2$, initiation by dissociation of hydrogen (or steam) and termination by atom (or atom-radical) recombinations have been shown to be in substantial, although not complete, agreement with the data.

Introduction

An examination of literature concerning the kinetics of the reactions which comprise the "water–gas equilibrium" shows disagreement among the various investigators with regard to the occurrence of a homogeneous reaction in silica vessels within the temperature range of 600 to 900°.[2a–5]

However, the considerable data from combustion and explosion experiments show that at somewhat higher temperatures reactions in the gas phase proceed with sufficiently high velocities that the "water–gas equilibrium" is established within extremely short time intervals.[6–10]

There is nowhere available sufficient evidence upon which to postulate reaction mechanisms, although the need for this information has long existed.

The objectives of the present work may be enumerated as follows: (1) to ascertain whether or not reaction between carbon monoxide and steam (as well as carbon dioxide and hydrogen) takes place to an appreciable extent in quartz vessels within the temperature range of 800 to 1100°; (2) to determine whether or not such reaction as may occur is predominantly of a homogeneous character; (3) to obtain sufficient kinetic data to evaluate a spe-

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[1] This research was supported in whole or in part by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

[2] (a) G. Hadman, C. Hinshelwood and H. Thompson, *Proc. Roy. Soc.* (*London*), **A137**, 87 (1932); (b) O. Ingles, *Trans. Faraday Soc.*, **48**, 706 (1952).

[3] E. Doehlmann, *Z. Elektrochem.*, **44**, 178 (1938).

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[5] F. Long and K. Sykes, *Proc. Roy. Soc.* (*London*), **A215**, 111 (1952).

[6] H. Passauer, *Z. physik. Chem.*, **161A**, 299 (1932).

[7] F. Haber and F. Richardt, *Z. anorg. Chem.*, **38**, 5 (1904).

[8] M. Vanpee and J. Samain, *Ann. Mines Belg.*, **5**, 630 (1952).

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[10] H. Dixon, *Phil. Trans. Roy. Soc.*, **175**, 617 (1884).

cific reaction rate expression and, if possible, to advance a concordant reaction mechanism.

Experimental

It became apparent early that for both the carbon monoxide–steam and carbon dioxide–hydrogen systems reaction proceeded rapidly enough to make mandatory the use of a flow technique. Accordingly, a cylindrical reaction vessel, designed to achieve rapid heating and cooling of the reactants, was fabricated from transparent quartz. The vessel dimensions, 3.4 cm. in diameter and 6.4 cm. in length, corresponded to the optimum "cyclone mixer" design[11] and therefore constituted a stirred flow reactor.

Tangential entry and exit of the gas stream from the vessel ensured complete "sweeping" of the free space. Entrance and exit leads of 2-mm. capillary tubing, 17 cm. in length, were chosen for most advantageous heating (and cooling) and to minimize the residence time of the gases in the regions of greatest temperature gradient. Of the total volume of the vessel, approximately 1% was contributed by the volume of the leads. The two thermocouple sheaths permitted a measurement of the temperature profile along the major axis of the reactor.

An identical vessel was constructed and packed with one cm. lengths of quartz tubing, sufficient to increase the surface area threefold, for use in certain of the experiments.

The vessel was situated in the center of a twelve-inch electrically heated furnace. By means of a Control Potentiometer, the temperature at the center of the reaction vessel was maintained within ±0.5°. Measurements made at other points along the principal axis of the vessel showed that the temperature of the gas increased about 10° in passing from entrance to exit. The temperature was measured with a Bureau of Standards calibrated platinum, 10% rhodium–platinum thermocouple.

Commercially available gases were taken from cylinders and suitably purified before being metered into the reaction system through capillary tube flowmeters which had been calibrated for the individual gases.

Mass spectrometric analyses of the purified gases showed the only remaining impurities to be nitrogen and argon. In particular, it was verified that the purification methods effectively eliminated oxygen from the reacting mixture. This was found to be imperative since small quantities of oxygen (about 1%) accelerated the reaction rates as much as 100-fold.

Steam was generated in a Dewar flask immersed in a steam-bath by means of an immersion heater to which the power supply was regulated by a rheostat and measured with a watt-meter. Steam condensation between generator and analytical system was prevented by heating electrically the connecting tubing.

Since a mass spectrometric analysis of the gas stream emerging from the reactor excluded the possibility of any interaction of the reactants with the nitrogen diluent or with one another to produce hydrocarbons, reaction may be expressed stoichiometrically by the equilibrium

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (1)$$

Therefore, the composition of the emergent gaseous mixture can be determined uniquely by the analysis of a single component.

It proved to be most advantageous to follow the rate of the carbon dioxide–hydrogen reaction by collecting the resulting steam in a calcium chloride absorption tube. Likewise, the rate of reaction of carbon monoxide and steam was measured by absorbing the carbon dioxide produced upon ascarite, after first removing the excess steam with calcium chloride.

By inclusion of suitable quantities of nitrogen the total flow rates were kept at 1200 ml./min. (1 atm., 20°), except for the runs in which the reaction time was deliberately varied. This flow rate corresponded to a reaction time of about 0.53 second, the volume of the reaction vessel being about 43 ml. The total pressure in the reaction vessel was approximately 800 mm. in all experiments.

With the exception of experiments in which temperature was varied for the purpose of determining activation energies, the temperature at the center of the vessel was maintained at 900.0 ± 0.5°.

The choice of temperature and reaction time was governed by the desire to limit the extent of reaction to about 1%, thus effectively eliminating the possibility of any "reverse" reaction. At 900° and 0.53 second reaction time the extent of reaction ranged from 0.5 to 2%, depending upon the reactant concentrations.

Results

Carbon Dioxide–Hydrogen Reaction.—An investigation was made of the relationship between extent of reaction and reaction time using carbon dioxide and hydrogen, each at a pressure of 0.50 atm. Partial pressures of steam in the effluent were used as a measure of the percentage reaction. Figure 1 indicates how closely the data approximate a direct proportionality between reaction time and extent of reaction. The apparent induction period, which cannot be attributed to the uncertainty of the data, suggests the roles of atoms and radicals in the reaction mechanism.

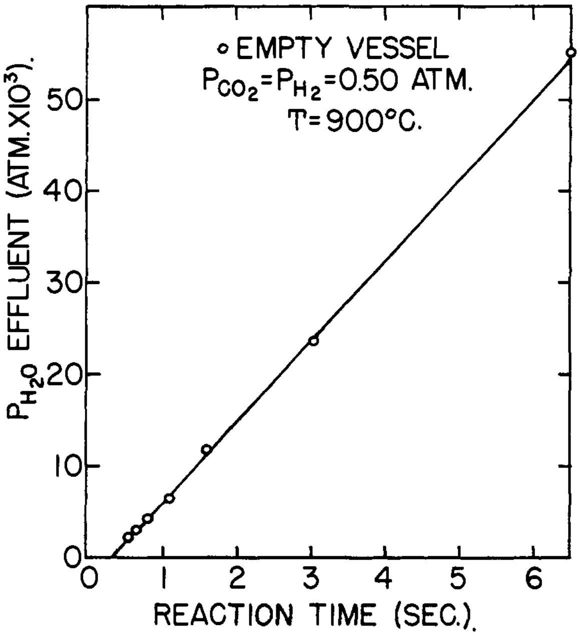

Fig. 1.—Effect of reaction time on rate of CO_2–H_2 reaction.

The dependence of reaction rate upon pressures of individual reactants was next ascertained. Experiments were carried out in both packed and empty vessels with the results shown in Figs. 2 and 3. Such close agreement between reaction rates in the two vessels, one having threefold greater surface area than the other, furnishes strong argument for a homogeneous gas phase process.

Dependence of the rate upon pressure of hydrogen was determined by making a series of runs in which a pressure of 0.50 atm. of carbon dioxide was maintained. In Fig. 2 pressures of steam in the effluent are plotted against the square roots of corresponding pressures of hydrogen in the reactant mixtures. Over the entire twenty-fold variation in hydrogen pressure a half-order dependence is followed.

While maintaining a constant pressure of hydrogen of 0.50 atm. the pressure of carbon dioxide was varied and the effect upon the reaction rate was ascertained. For a tenfold variation of the pressure

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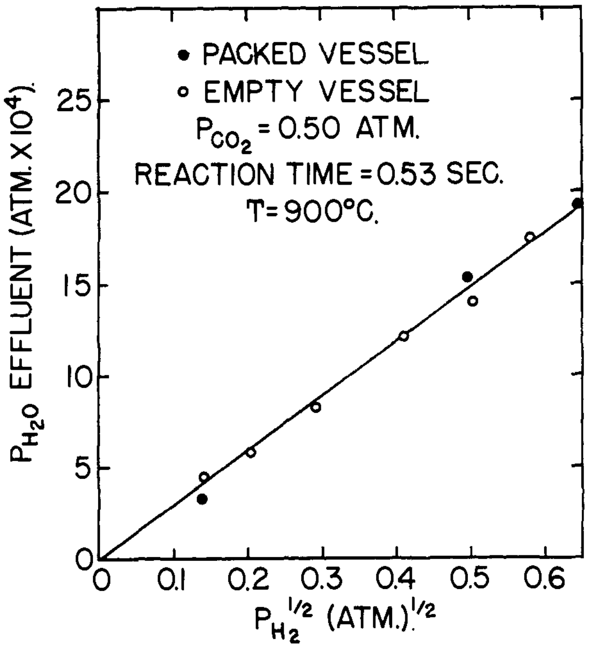

Fig. 2.—Effect of H_2 pressure on rate of CO_2–H_2 reaction.

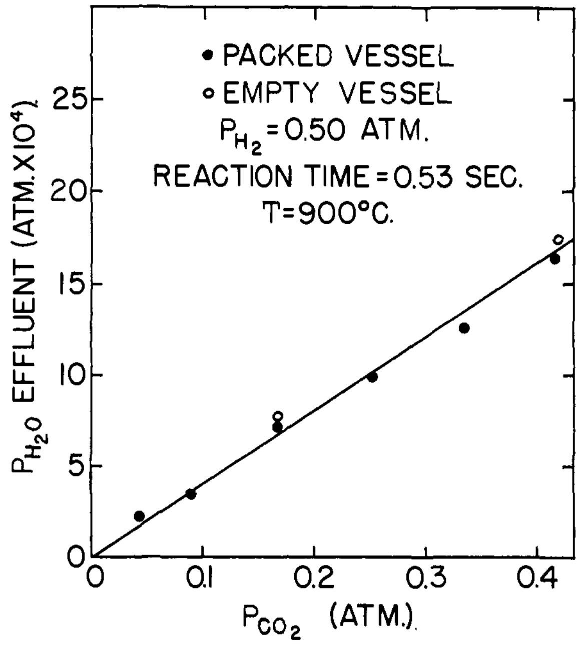

Fig. 3.—Effect of CO_2 pressure on rate of CO_2–H_2 reaction.

of carbon dioxide the final pressure of steam obeys a first-order dependence, as is seen in Fig. 3.

A study was made of the effect upon the reaction rate of adding varying amounts of carbon monoxide to the initial mixture of carbon dioxide and hydrogen, each at 0.33 atm. pressure, in the packed vessel. Results shown in Fig. 4, in which the reciprocals of the partial pressures of steam in the effluent have been plotted against the corresponding carbon monoxide pressures in the reactant mixtures, indicate that carbon monoxide has a distinct inhibiting effect upon the rate of reaction.

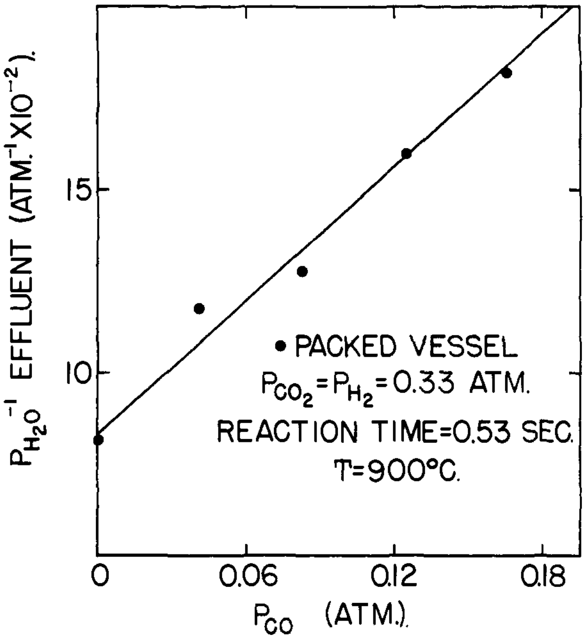

Fig. 4.—Effect of CO pressure on rate of CO_2–H_2 reaction.

At this point the available data are in accord with a rate expression of the form

$$d/dt[H_2O] = \frac{k_1[H_2]^{1/2}[CO_2]}{1 + A[CO]} \tag{2}$$

where k_1 and A are appropriate constants. For calculating the values of k_1 corresponding to each rate measurement A was given the arbitrary value of 3.6×10^3 l. mole^{-1}. The indifference of k_1 to the presence or absence of packing in the vessel was noted.

Use of the differential form of the rate equation and the initial concentrations of reactants in calculating k_1 is justified, since in none of the experiments did reaction proceed farther than 2% of completion.

Furthermore, it was demonstrated in Fig. 1 that below 11% reaction the extent of reaction varied linearly with reaction time.

The temperature coefficient of this reaction was determined with a series of runs using the packed vessel in which the pressures of carbon dioxide and hydrogen were 0.50 atm. and the reaction time was 0.50 second. Rate measurements were made at eight temperatures between 875 and 1050°. A plot of the logarithms of the previously defined rate constants, k_1, against the reciprocals of the corresponding absolute temperatures yields a straight line (Fig. 5) from the slope of which an activation energy of 57.0 kcal./mole is calculated.

By combining the average value of k_1 from 22 experiments at 900° (0.43 l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$) with the experimentally determined activation energy the observed rate constant for the reaction of carbon dioxide and hydrogen is found to be

$$k_1 = 9.5 \times 10^{10} \exp(-57000/RT)\text{liters}^{1/2}\text{ moles}^{-1/2}\text{ sec.}^{-1} \tag{3}$$

Carbon Monoxide–Steam Reaction.—For the carbon monoxide–steam system experiments were

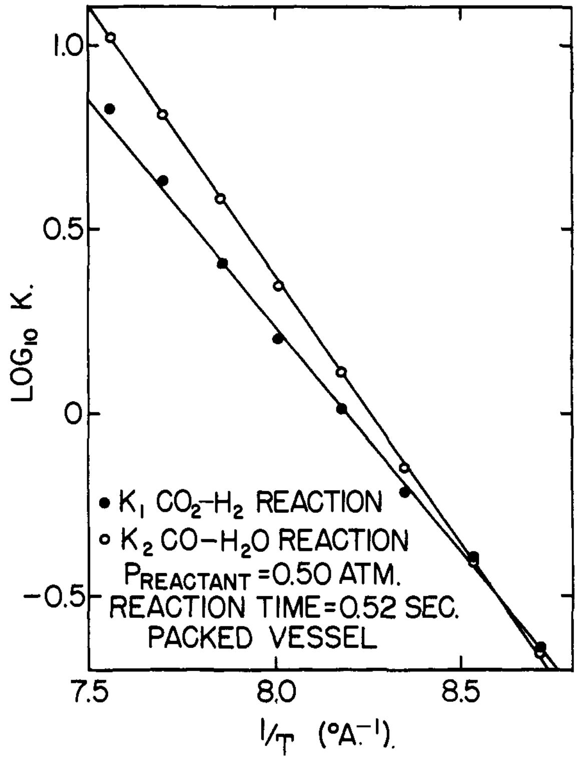

Fig. 5.—Effect of temperature on rates of CO_2–H_2 and CO–H_2O reactions.

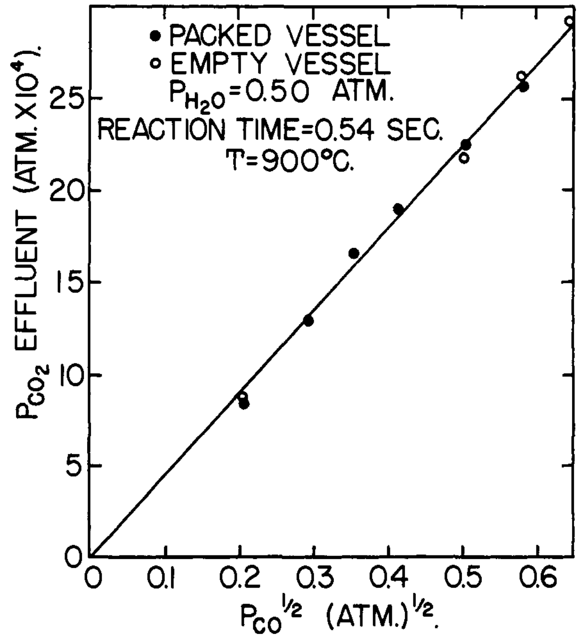

Fig. 6.—Effect of CO pressure on rate of CO–H_2O reaction.

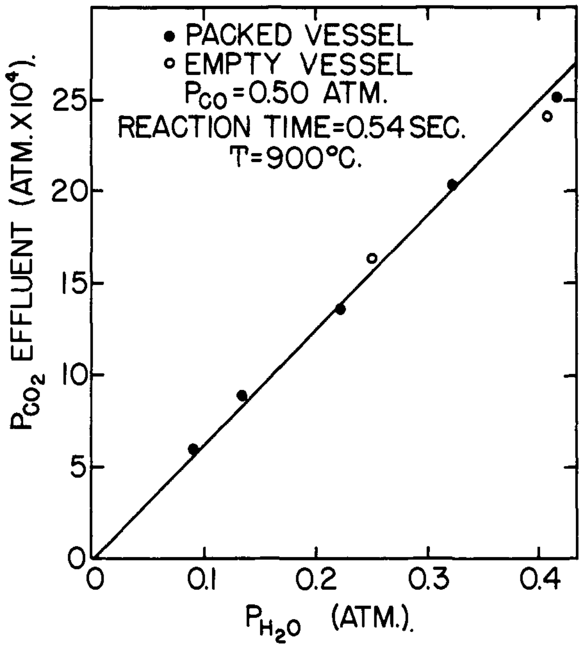

Fig. 7.—Effect of H_2O pressure on rate of CO–H_2O reaction.

designed to determine the apparent order of the reaction with respect to carbon monoxide, steam and hydrogen. Both packed and empty vessels were used with no apparent changes in the rate of reaction, as is evident in Figs. 6 and 7.

In the first series of runs the pressure of steam was constant at 0.50 atm. and the initial pressures of carbon monoxide were varied over a tenfold range. A one half-order dependence of the rate upon carbon monoxide pressure is indicated by Fig. 6, in which pressures of carbon dioxide in the effluent are plotted against the square roots of the pressures of carbon monoxide.

Figure 7 shows a plot of the final carbon dioxide pressures against initial pressures of steam for runs at a constant pressure of 0.50 atm. of carbon monoxide. Over a fourfold variation in the steam pressures a first-order dependence is quite apparent.

Hydrogen retards the reaction rate, but in a manner dissimilar to that of carbon monoxide in the previous reaction, as may be seen in Fig. 8 where the reciprocals of the carbon dioxide pressures in the effluent have been squared and plotted against the corresponding hydrogen pressures in the reactant mixtures. Runs were made in the empty vessel, with constant pressures of carbon monoxide and steam of 0.33 atm. and over an eightfold variation in the hydrogen pressure.

The data are adequately represented by the following rate equation

$$d/dt[CO_2] = \frac{k_2[CO]^{1/2}[H_2O]}{(1 + B[H_2])^{1/2}} \qquad (4)$$

k_2 and B being suitable constants.

For calculating the values of k_2 a value of 1.2×10^4 l. mole^{-1} has been arbitrarily assigned to B. The calculated quantities, k_2, do not deviate greatly from the average value, obtained from 23 measurements at 900°, of 0.65 l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$. No trends which might be attributed to increased surface within the vessel are apparent.

The effect of temperature variation upon the rate constant has been obtained from results of a series of eight runs using the packed vessel at temperatures ranging from 875 to 1050°. The pressure of each reactant was 0.50 atm. and the reaction time was 0.54 second for each run.

From the usual Arrhenius-type plot (Fig. 5) an activation energy of 67.3 kcal./mole has been calculated.

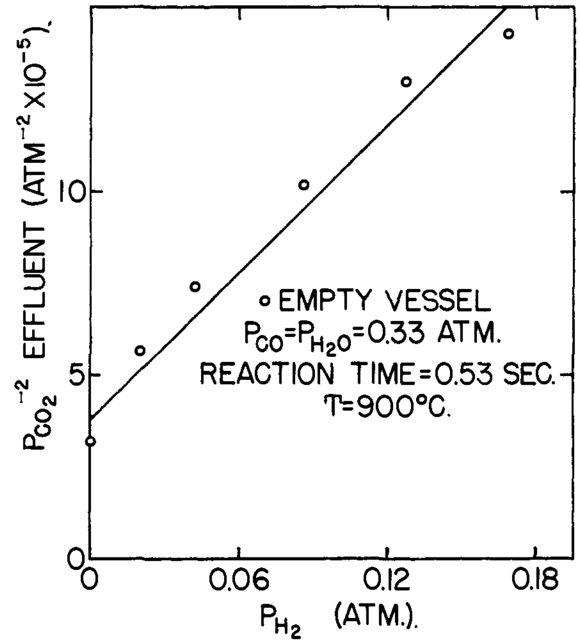

Fig. 8.—Effect of H_2 pressure on rate of CO-H_2O reaction.

The observed rate constant for the reaction of carbon monoxide and steam, calculated in the same manner as k_1, is given by the expression

$$k_2 = 5.0 \times 10^{12} \exp(-67300/RT)\text{liters}^{1/2}\ \text{moles}^{-1/2}\ \text{sec.}^{-1} \quad (5)$$

Discussion

The single remaining objective is the formulation of reaction mechanisms which will yield the experimentally observed rate expressions. In searching for such mechanisms consideration must be given to the experimental observations which point toward entirely homogeneous processes, some of which involve atoms and radicals. Although no direct experimental proof that the reactions proceed by chain mechanisms is offered, the large acceleration of the reaction rates by traces of oxygen is most easily explained if the mechanisms involve chains.

Chain reactions, first proposed by Bradford,[12] give rise to rate expressions which, with limitations, are in accord with those obtained directly from the experimental data.

Although various chain initiating and terminating steps have been used, the chain propagating reactions in Bradford's mechanisms have been employed by several investigators of the "water–gas" reactions. Kondratjev and Ziskin[4] included them in the mechanism which they submitted to explain the results of their study of the carbon dioxide–hydrogen reaction in the presence of small amounts of oxygen. Behrens[13] made use of them in his theory of the reaction mechanism based upon data for the "freezing-in" of the "water–gas" equilibrium. Ingles,[2b] in studying the reaction of carbon monoxide and steam upon carbon, found them to be useful in explaining his results.

The gas phase dissociation of hydrogen molecules at about 600° has been chosen by Cullis and Hinshelwood[14] as the chain initiating process in the hydrogen–oxygen reaction between the second and third explosion limits.

Passauer[6] concluded that dissociation of steam at temperatures between 500 and 800° was responsible for rapid attainment of the "water–gas equilibrium" in the "preheating zone" of carbon monoxide–air flames.

For the reaction of carbon dioxide and hydrogen Bradford's[12] mechanism takes the form

$$H_2 + M \xrightarrow{k_3} 2H + M \quad \text{initiation} \quad (6)$$

$$H + CO_2 \underset{k_5}{\overset{k_4}{\rightleftarrows}} OH + CO \quad \text{propagation} \quad (7)$$

$$OH + H_2 \underset{k_7}{\overset{k_6}{\rightleftarrows}} H + H_2O \quad \text{propagation} \quad (8)$$

$$2H + M \xrightarrow{k_8} H_2 + M \quad \text{termination} \quad (9)$$

M being any molecule in the gaseous phase.

If a stationary-state concentration of hydroxyl radicals and equal rates of chain initiation and termination are assumed the measured reaction rate, given by the rate of production of steam, may be represented by the expression

$$d/dt[H_2O] = k_3^{1/2}k_8^{-1/2}[H_2]^{1/2} \times \frac{k_4k_6[CO_2][H_2] - k_5k_7[CO][H_2O]}{k_6[H_2] + k_5[CO]} \quad (10)$$

When applied to the experiments which are of interest here the second term in the numerator may be neglected, thus reducing the above expression to

$$d/dt[H_2O] = \frac{k_3^{1/2}k_8^{-1/2}k_4[H_2]^{1/2}[CO_2]}{1 + k_5k_6^{-1}[CO]/[H_2]} \quad (11)$$

which is quite similar in form to equation 2.

Under the experimental conditions of constant high concentrations of carbon dioxide and hydrogen, the observed manner of retardation of the reaction rate by carbon monoxide is that which would be expected from equation 11.

In the absence of added carbon monoxide the denominator of equation 11 is effectively unity, if k_5 and k_6 are assumed to be of approximately equal magnitude, in agreement with the observed half-order and first-order dependence of the reaction rate upon hydrogen and carbon dioxide pressure, respectively.

Equation 11 requires the following relationship between the observed activation energy, E_1, and the activation energies for individual steps in the mechanism

$$E_1 = E_4 + {}^1/_2(E_3 - E_8) = E_4 + {}^1/_2\Delta E_H \quad (12)$$

where ΔE_H is the dissociation energy of the hydrogen molecule and E_4 the activation energy of step 4 in the reaction mechanism.

Lewis and von Elbe[15] give a value for ΔE_H of 103 kcal. By combining their calculated value of 25 kcal. for the heat of reaction 7 with Avramenko

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(12) B. Bradford, *J. Chem. Soc.*, 1557 (1933).

(13) H. Behrens, *Z. physik. Chem.*, **195**, 24 (1950).

(14) C. Cullis and C. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A186**, 462 (1946).

(15) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, Appendix.

and Lorentso's[16] activation energy of 7 kcal. for the reverse process to obtain E_4, one may use equation 12 to calculate E_1. The calculated activation energy of 84 kcal. differs considerably from the observed value of 57 kcal.

When applied to the reaction of carbon monoxide and steam Bradford's[12] mechanism may be expressed as

$$H_2O + M \xrightarrow{k_9} OH + H + M \quad \text{initiation} \quad (13)$$

$$OH + CO \underset{k_4}{\overset{k_5}{\rightleftarrows}} H + CO_2 \quad \text{propagation} \quad (14)$$

$$H + H_2O \underset{k_6}{\overset{k_7}{\rightleftarrows}} OH + H_2 \quad \text{propagation} \quad (15)$$

$$H + OH + M \xrightarrow{k_{10}} H_2O + M \quad \text{termination} \quad (16)$$

where M is any molecule in the gaseous phase.

Again, by assuming stationary-state concentrations of hydroxyl radicals and hydrogen atoms, as well as that the chain initiating and terminating reactions are proceeding with equal velocities, it is possible to combine the rates of individual reactions in the mechanism to yield an expression for the measured rate of reaction.

$$d/dt[CO_2] = k_9{}^{1/2}k_{10}{}^{-1/2}[H_2O]^{1/2} \times \frac{k_5k_7[CO][H_2O] - k_4k_6[CO_2][H_2]}{(k_5[CO] + k_6[H_2])^{1/2}(k_4[CO_2] + k_7[H_2O])^{1/2}} \quad (17)$$

The terms involving $[CO_2]$ may be neglected when applying the above expression to experiments reported here; therefore, it may be rewritten as follows

$$d/dt[CO_2] = \frac{k_9{}^{1/2}k_{10}{}^{-1/2}k_7{}^{1/2}k_5{}^{1/2}[CO]^{1/2}[H_2O]}{(1 + k_6k_5{}^{-1}[H_2]/[CO])^{1/2}} \quad (18)$$

The similarity between equations 18 and 4 is evident.

When the pressures of carbon monoxide and steam do not vary, equation 18 is in accord with the observed manner of retardation of the reaction rate by hydrogen. Likewise, when no hydrogen is added the observed first-order and one half-order dependences of the rate upon steam and carbon monoxide, respectively, are consistent with equation 18 if the previous assumption with regard to k_5 and k_6 is valid.

Just as equation 12 followed from 11, so does equation 19 from 18.

$$E_2 = {}^1/_2(E_9 - E_{10} + E_7 + E_5) = {}^1/_2(\Delta E_s + E_7 + E_5) \quad (19)$$

where E_2 is the observed activation energy, ΔE_s is the energy of dissociation of steam to yield a hydrogen atom and a hydroxyl radical, E_7 and E_5 are activation energies for steps 7 and 5, respectively, in the reaction mechanism.

Lewis and von Elbe's[15] data may be used to obtain a value of ΔE_s of 118 kcal. and a heat of reaction 8 of 15 kcal. These data, together with Avramenko and Lorentso's[16] activation energies (E_5 = 7 kcal., E_6 = 10 kcal.), yield a calculated value E_2 of 75 kcal. Agreement with the experimental result of 67 kcal. is satisfactory.

In addition to the discrepancy between the observed and estimated values of E_1 it may be noted that although the mechanisms require of the constants, A and B, that one be the reciprocal of the other the selected values are 3.6×10^3 and 1.2×10^4, respectively; however, the choice is not critical since the rate constants are rather insensitive to changes in these parameters.

It should be apparent that the data, although certainly constituting no proof of the chosen mechanisms, are in no serious disagreement with the mechanistic requirements.

A number of additional observations can be made regarding the correlation of data for the two reactions; however, it should be remembered that the rate expressions and mechanisms apply to the initial stages of the reactions where chain initiating and terminating steps of prominence near equilibrium may be of negligible importance.

Although the difference between the observed activation energies is at variance with the known heat of reaction 1, for which the value of −7.9 kcal. at 900° has been interpolated from the data of Wagman, Kilpatrick, Taylor, Pitzer and Rossini,[17] the difference between the calculated values of E_1 and E_2 (9 kcal.) is in apparent agreement with their value of ΔH_0^0 of −9.6 kcal.

Similarly, the experimental rate constant ratio, $k_2/k_1 = 1.51$, is only moderately in agreement with the interpolated value of the equilibrium constant of reaction 1 (0.753 at 900°) taken from the data of Wagman, *et al.*,[17] but the rate expressions which result from the assumed mechanisms combine to yield the correct equilibrium quotient if assumptions are made with regard to the relative magnitudes of the four rate constants for the chain propagating steps.

This investigation, although incomplete, since it has been experimentally feasible to study the effect of only one product upon each reaction rate, has yielded kinetic information concerning the "water-gas" reactions remote from equilibrium.

PRINCETON, NEW JERSEY

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[16] L. Avramenko and R. Lorentso, *Zhur. Fiz. Khim.*, **24**, 207 (1950).

[17] D. Wagman, J. Kilpatrick, W. Taylor, K. Pitzer and F. Rossini, *J. Research Natl. Bureau Standards*, **34**, 143 (1945).