Remarks on Evaluating Kinetic Data for Technical Purposes

OTTO STELLING and OTTO von KRUSENSTIERNA

Division of Applied Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden

The chemical engineer studying the kinetics of catalyzed reactions is often unaware of the limitations of his experimental method and uses hidden parameters which diminish the value of his data. The Langmuir-Hinshelwood method, the Hougen-Watson method and the exponential equations of Temkin are critically discussed. The conclusion is that, independant of the choice of adsorption isotherm, the same rate equation can be derived. The backward rate expression cannot be derived exactly from the forward rate expression but some restrictions on the form of the backward rate expression can be obtained with the help of Horiuti's "stoichiometric numbers". Some often occurring weak points in kinetic investigations are summarized and a standard procedure for kinetic investigations is outlined and illustrated with an experimental investigation of the watergas-shift reaction.

The processing techniques of the chemical industry show now a very marked tendency to change from the classical discontinuous processes as those of the dye industry to modern continuous processes exemplified by the petrochemical industry. These modern processes are often based on heterogeneous catalysis and the desired product is obtained by the use of the highest possible accuracy in the process control. This change in the industry has been made possible by a better general knowledge of the processes and especially by a more detailed understanding of all the kinetic problems involved. These problems have to be solved before a calculation of the engineering equipment of a process can start. If kinetics is defined as including both the chemical processes and the physical processes of mass- and heat-transfer one is bound to state that the branch of kinetics has a dominating position in modern chemical engineering research.

The chemical engineer and the research-chemist approach the problems of heterogeneous kinetics from two different sides. The chemical engineer is usually satisfied if he can find a rate equation reliable enough to permit reactor calculations and process control in the practical working range of pressures and temperatures. The research-chemist on the other hand wants to find the reaction mechanism itself with the help of experimental kinetic data and

tries to determine the simple primary reaction steps from which the complicated total reaction is built up. The distance between these two outlooks has been lessening during the last decades in as much as the interest of the chemical engineer is changing into a more exact knowledge of the mechanism of a reaction and its bearings on process possibilities and catalyst characteristics. The exact determination of the reaction mechanism in detail to its primary steps is, however, still very difficult and even such simple classical reactions as the oxidation of hydrogen and of carbon monoxide are still debated.

The main difficulty in mechanism determinations is often the experimental accuracy which is too limited to determine the often very small differences between different reaction mechanisms. This means that it usually pays back to invest work in increasing the experimental accuracy and to use an experimental approach that gives crucial data rather than general ones which are used for calculations based on more or less plausible mechanisms. On the other hand, as Christiansen [1] recently has pointed out, an *underestimation* of the accuracy can lead to serious consequences when data are used to fit a chosen mechanism.

Many different experimental methods and methods of data evaluation have been used in the study of kinetics and it is easy to understand that sometimes kineticists have been unaware of the limitations in their experimental method. Very often hidden parameters make the general treatment of valuable experimental data impossible. An often occurring case is the laboratory chemist who neglects the importance of diffusion processes and produces data which have only a limited value outside the laboratory. The chemical engineer on the other side often makes too far reaching conclusions about the nature of the plausible reaction mechanism which fits his data.

With these views in mind we have thought it to be of some value to discuss critically some of the methods which usually have been used for the kinetic investigations of heterogeneous processes of technical interest. In connection with this discussion we propose a standard procedure to be followed in investigations of this kind and which perhaps could help to diminish the confusion which one encounters in the current literature. As an example of this procedure we finally give some data from a kinetic investigation of the watergas-shift reaction.

THE LANGMUIR-HINSHELWOOD METHOD

The classical Langmuir-Hinshelwood method has in many cases given a good qualitative and sometimes also a quantitative explanation of experimental data by an assumed reaction mechanism. A reaction of the type

$$A + B = R + S$$
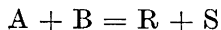
is studied by measuring the conversion at different partial pressures p_A while the other partial pressures are kept constant. If a low conversion is chosen the consumed and produced amounts of A, B, R and S are so small that the initial pressures p_A, p_B, p_R and p_S need to be only very slightly corrected. When reversible reactions are studied it is usually convenient to chose pressure conditions so that the backward reaction can be neglected.
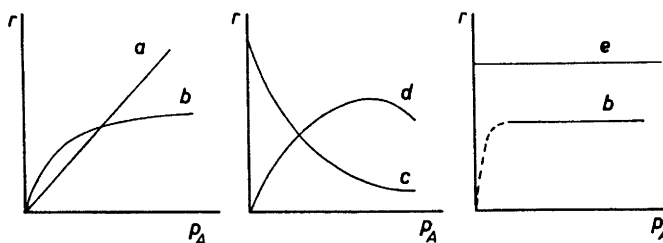
Fig. 1. The rate of reaction, r, as a function of the partial pressure p_A when p_B, p_R and p_S are constant. Each curve a—e corresponds to a Langmuir-Hinshelwood mechanism (Eqns. 1a—1e).

If for instance the rate of the forward reaction r_f and its variation with p_A is investigated, the experimental data often can be correlated with one of the following equations graphically represented in Fig. 1 (curves a—e).

$$r_f = kp_A \quad \text{(1a)}; \qquad r_f = kp_A/(b + K_Ap_A) \quad \text{(1b)}; \qquad r_f = k/(c + K_Ap_A) \quad \text{(1c)};$$
$$r_f = kp_A/(d + K_Ap_A)^2 \quad \text{(1d)}; \qquad r_f = k \quad \text{(1e)};$$

The following mechanisms can be derived from these different cases with the Langmuir-Hinshelwood method: Eqn. (1a) shows that the rate is proportional to the number of collisions of A with the active catalyst surface. Eqn. (1b) shows that the rate is proportional to that part of the active surface which is covered with adsorbed A. Eqn. (1c) shows that the rate is dependant on the part of the surface that is not covered with A and that A acts as an inhibitor. Eqn. (1d) shows that the rate is proportional to the product of two adsorbed substances one of which is A. Finally eqn. (1e) shows that the rate is independant of A. This can be interpreted as an mechanism in which A is not involved or that A is so strongly adsorbed — eqn. (1b) — that $K_Ap_A \gg b$.

The same measurements are performed with the other gascomponents and finally the rate can be expressed as a function of all the involved reactants and products, *i.e.*

$$r_f = f[(p_A), (p_B), (p_R), (p_S)]$$

This function can then, after closer inspection of the involved constant pressures, be written in the form of a rate equation.

Assume for instance that the experimental data have resulted in $r_f = f[(p_A), (p_B/(b+K_Bp_B)), (1/(c+K_Rp_R), (p_S)^\circ]$
and that closer examination of the constants b and c has revealed the connections $q = 1 + K_Rp_R$ and $c = 1 + K_Bp_B$. The rate equation can then be formulated

$$r_f = k \; p_Ap_B/(1 + K_Bp_B + K_Rp_R)$$

This equation should describe the reaction rate for the experimental conditions as well as the rate of the forward reaction when the reactants are converted simultaneously in the technical process. The equivalent mechanism is the collision of A, from the gas phase, with adsorbed B as the slowest and rate determining step and with the product R partly covering the active surface and therefore diminishing the rate.

Technical investigations often only determine the rate of the forward reaction but for some reversible reactions as the NH_3-synthesis, the SO_2-

oxidation etc., the total rate must be determined. The backward rate r_b is then evaluated in the same manner as r_f and the total (net) rate becomes

$$r = r_f - r_b$$

The experimental apparatus used in connection with the Langmuir-Hinshelwood method have been both of the static and of the flow-system type. In modern investigations, however, the flow system is preferred as it gives defined diffusion conditions and very often a higher accuracy of analysis.

An excellent example of the Langmuir-Hinshelwood method applied to a technical process is the investigation of Gadsby, Hinshelwood and Sykes [2] and the following investigations [3-5] of the complicated system steam-carbon with four different simultaneous reactions.

THE HOUGEN-WATSON METHOD

An extension of the Langmuir-Hinshelwood approach has been developed by Hougen and Watson [6] and Hougen and Yang [7] and this method has often been used during the last decade mostly in the U.S.A. for the kinetic investigation of technical processes.

The Hougen-Watson method uses an elegant formal way of expressing the chemisorption of a gas on the active catalyst surface and together with other simplifications is it possible to derive the rate equation for every possible reaction mechanism with a minimum of calculations.

The Hougen-Watson method can, for instance, be used to derive the rate equation for the mechanism of the before mentioned example. The first reaction step is assumed to be the collision of A from the gas-phase with B adsorbed on the surface. The products formed are adsorbed R and S in the gas-phase. If the adsorptions of B and R are fast in comparison with the first step, they can be treated as adsorption equilibria and the first step becomes rate determining. The rate of the reversed reaction is then the collision of S with adsorbed R.

The concentrations of the adsorbed particles are represented by c_B and c_R, the concentration of free active centers by c_l and the total concentration of active centers by L. The chemisorption can then be written as a chemical reaction between a gas particle and an active center 1. In this case

$$B + 1 = Bl \qquad R + 1 = Rl \qquad A + Bl = Rl + S$$
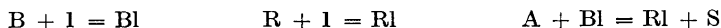
where the last expression constitutes the rate determining step. The rate, the adsorption equilibria and the surface-concentrations can now be written

$$r = k_1 p_A c_B - k_2 p_S c_R$$
$$K_R = c_R/p_R c_1 \qquad K_B = c_B/p_B c_1$$
$$L = c_1 + c_B + c_R$$

The elimination of the unknown surface-concentrations gives the rate equation expressed in the measurable partial pressures

$$r = \frac{k_1 K_B(p_A p_B - (1/K)p_R p_S)}{1 + K_B p_B + K_R p_R}$$

where K is the equilibrium constant for the reaction. For the forward reaction this

expression is identical with the one in the foregoing example. However, this rate equation could have been written directly with the help of formula tables which have been constructed by Hougen and Yang [7] *.

The formal ease with which the different rate equations can be derived has often influenced the experimental approach when the Hougen-Watson method is used.

The reaction rates are measured with an isothermal flow-reactor for which the general equation holds

$$F \ \mathrm{d}x = r \ \mathrm{d}W$$

where F = feed (mole) / (min), $\mathrm{d}x$ = conversion (mole) / (mole F), $\mathrm{d}W$ = mass catalyst (g) and r = rate (mole) / (g catalyst) (min). Other units, dimensionally consistent, could of course be used. If diffusion is not a limiting factor a differential reactor (small catalyst bed, low conversion) or an integral reactor (large catalyst bed, high conversion) can be used and the rates would be, respectively

$$r_{\mathrm{diff}} = (\Delta x/\Delta W) \ F \qquad\qquad r_{\mathrm{int}} = \mathrm{d}x/(\mathrm{d}W/F)$$

For the integral-reactor the rate is the tangent to the experimentally determined function $x = \mathrm{f}(W/F)$ and can be calculated by graphical derivation. By variation of the partial pressures, usually in a restricted range, as compared to the Langmuir-Hinshelwood-method, a number of r-values are produced.

The next step is to derive all the theoretical possible rate mechanisms and their equivalent rate equations. In this way as much as $75-100$ equations can be set up [8] but this number can often be reduced to $10-20$ by an inspection of initial-rate data. Hougen and Yang [7] have demonstrated useful relations between the initial rate, the pressure and the mole fractions for different rate equations which are similar to the curves in Fig. 1.

After this test the constants of the remaining equations are determined graphically or by the method of least-squares. Equations with negative constants are eliminated as being physically unsound and the last $3-4$ equations usually show a good fit to the experimental data. The last decision is often difficult but a comparison of the integrated equation with data from an integral-reactor can usually be helpful. An unnormal variation of the constants with temperature can also be used for the elimination of equations.

Apart from the mentioned original articles [6,7] the Hougen-Watson method has been presented in some textbooks [9,10] and the calculations involved have been discussed in detail by Corrigan [11].

THE VALIDITY OF THE LANGMUIR-HINSHELWOOD AND THE HOUGEN-WATSON METHODS

Recently the LH- and the HW-methods have been critically discussed by Weller [12] and Boudart [13] and the use of the HW-method in technical investigations has been questioned. Weller points out that the Langmuir adsorption isotherm, which is the base of both methods, has been derived with the assumption of a constant heat of adsorption independant of the surface coverage. However, experiments always show a decreasing heat of adsorption with increasing coverage. This interaction of adsorbed molecules or atoms has also been observed when several gases are adsorbed simultaneously. The

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* For the example treated here a misprint in the original work, Table 4, has led to a misleading discussion of initial-rate effects for this case, p. 154 and Table 5.

adsorption of one gas can sometimes increase the adsorption of another gas. If the adsorption of A increases when B also is adsorbed the amount of adsorbed A, c_A, can according to Weller be expressed in the following form:

$$c_A = kp_A/(1 + K_A p_A - K_B p_B)$$

This expression has a negative adsorption-constant which in the Hougen-Watson-method was a characteristic mark of physically unsound rate equations which therefore were ruled out.

According to Weller the Langmuir-Hinshelwood method should be used with care and only for qualitative considerations. The Hougen-Watson method should be used as a purely empirical method for data-fitting and as a method by which a mechanism can be determined "which the unwary investigator is often led to believe that he has uniquely deduced".

Instead the use is recommended of exponential expressions of the form $r = k (p_A)^m (p_B)^n (p_R)^q$ . . . . . where the exponents have integral or half-integral values or zero. Weller demonstrates on several investigations described in the literature how a simple exponential expression with only one constant gives the same data fitting as complicated Hougen-Watson expressions with up to 4 constants. Rate equations of the simple exponential form can therefore with advantage be used for technical calculations.

The real difference between Wellers exponential expressions and the Langmuir-Hinshelwood and Hougen-Watson expressions is, however, not so large. It is a matter of choice of the adsorption isotherm. Weller uses indirectly the Freundlich isotherm and the other expressions are based on Langmuir.

Boudart [13] shows in a following article that the use of Langmuir's isotherm for non-ideal surfaces, "the paradox of surface catalysis", can be explained by the broad energy distribution of the active centers and also by the possible mathematical approximation

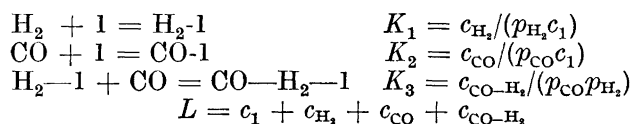$$\Theta_F = k \ p^n \approx \Theta_L = bp/(1 + bp)$$

This means that the pure empirical Freundlich isotherm, Θ_F with an exponential distribution of the heat of adsorption always can be approximated by an expression Θ_L of the same mathematical form as the Langmuir isotherm. This is of course the reason why Weller can fit his simple one-constant expressions with about the same deviations as those found with the Hougen-Watson method.

Some rate equations which are believed to be uniquely expressed in the exponential form must with the same argument be derivable from the Langmuir isotherm and Boudart shows how this can be done for the well-known Temkin-Pyzhev rate equation for the ammonia synthesis.

To sum up it can be said that the Langmuir isotherm, exactly valid only for ideal surfaces, can be used with advantage for the derivation of rate equations. It must be observed, however, that the involved constants are not real adsorption constants but rather a kind of average constants for the different "surfaces" of which a heterogeneous surface is made up. This is independant

of the real nature of the variation in the heat of adsorption, it may be due to surface heterogeneity, interaction between adsorbed particles or to some form of electron effects of the bulk of the catalyst.

Deviations from the normal adsorption mechanisms occur. As shown above Weller pointed out that mixed chemisorption sometimes can give effects which can be interpreted by negative adsorption constants. These cases of mixed chemisorption, so important for the understanding of heterogeneous catalytic processes, are still not very much investigated [14-16]. Most likely the observed effects are due to a kind of surface compounds ("adducts") and by this assumption it will be shown here how adsorption isotherms can be derived without the use of negative adsorption coefficients. Assume that the adsorption of CO is increased with increasing pressures of H_2 and that the surface compound CO-H_2-1 is produced. With the formal writing of the Hougen-Watson method:

$$H_2 + 1 = H_2\text{-}1 \qquad\qquad K_1 = c_{H_2}/(p_{H_2}c_1)$$
$$CO + 1 = CO\text{-}1 \qquad\qquad K_2 = c_{CO}/(p_{CO}c_1)$$
$$H_2\text{---}1 + CO = CO\text{---}H_2\text{---}1 \quad K_3 = c_{CO\text{-}H_2}/(p_{CO}p_{H_2})$$
$$L = c_1 + c_{H_2} + c_{CO} + c_{CO\text{-}H_2}$$

If the total amount of adsorbed CO is $C_{CO} = c_{CO} + c_{CO\text{-}H_2}$

then

$$C_{CO} = \frac{L\, K_2 p_{CO}}{\left(\dfrac{1 + K_1 p_{H_2}}{1 + \dfrac{K_3}{K_2} K_1 p_{H_2}}\right) + K_2 p_{CO}} \approx k\left(\frac{1 + \dfrac{K_3}{K_2} K_1 p H_2}{1 + K_1\, p H_2}\right)^m \left(K_2 p_{CO}\right)^m$$

If $K_3 > K_2$ the adsorbed amount of CO is increasing with increasing pressure p_{H_2} as observed and if $(K_3 K_1/K_2)p_{H_2} \gg 1$ the isotherm can be written $C_{CO} = k(p_{CO})^m (p_{H_2})^{am}$; $(0 < a,\ m < 1)$.
With the mechanism $H_2 + CO\text{---}1 = H_2\text{---}CO\text{---}1$, a similar simpler expression can be derived, $C_{CO} = k(p_{CO})^n(1 + K_2 p_{H_2})^n$; $(0 < n < 1)$.

Other forms that deviate from the normal Langmuir isotherm are derived from switch-mechanisms like

$$AB + 1 = B\text{---}1 + A \qquad or \qquad A + B\text{---}1 = A\text{---}1 + B$$

For instance the amount of adsorbed N_2 in Temkins mechanism for the ammonia synthesis, C_{N_2}, is obtained from the step:

$$2\ NH_3 + 2\ 1 = 2\ N\text{-}1 + 3\ H_2$$

$$C_{N_2} = k\ p_{NH_3}/\ (p_{H_2}^{1.5} + K^{0.5}\ p_{NH_3})^2$$
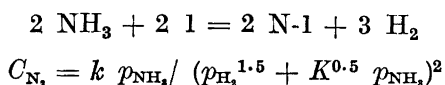
The large number of possible mechanisms makes an *a priori* derivation of every plausible mechanism impossible. In spite of this, technical investigations show a tendency to overestimate the calculating possibilities. It is not unusual

that some simple experimental series solve the problems faster and more reliable than tideous and unsure calculations of data fitting. A "most plausible" mechanism is often overvalued. As an example the work of Barkley, Corrigan, Wainwright and Sands [17] on the catalytic reversed shift reaction will be discussed.

They investigated the rate of the reaction $CO_2 + H_2 = H_2O + CO$ and found on the basis of a least-square treatment of plausible equations

$$r = k \frac{(p_{CO_2} p_{H_2} - p_{CO} p_{H_2O}/K)}{1 + K_A p_{CO_2} + K_R p_{CO}}$$

As the products CO and H_2O are produced in equivalent amounts and only CO_2 and H_2 are shown to have been experimentally varied in the feed, the experimental data could as well have been expressed by a rate equation with a denominator of the form $(1 + K_A p_{CO_2} + K_S p_{H_2O})$. This equation is founded on a mechanism which was not selected as plausible but seems to be more in accordance with other investigations [18,19].

THE TEMKIN METHOD

In their derivation in 1940 of the well-known rate equation for the ammonia synthesis, Temkin and Pyzhev [20] started with a non-ideal adsorption isotherm with a linear decrease of the heat of adsorption with coverage. The assumed mechanism was

$$N_2 \rightleftharpoons N_2\text{-ads} \qquad \text{(a)}$$

$$3 H_2 + N_2\text{-ads} = 2 NH_3 \qquad \text{(b)}$$

The adsorption of nitrogen (a) is rate determining and reaction (b) is assumed to be in equilibrium. The rate of the slow reaction is now the difference between the rates of adsorption and desorption or

$$r = k_a p_{N_2} e^{-g\Theta} - k_d e^{h\Theta}$$

The adsorption isotherm has the form

$$\Theta = \frac{1}{g+h} \ln a_0 p_{N_2}$$

The equilibrium (b) gives

$$P_{N_2}^* = (N_2\text{-ads}) = K_N \frac{(p_{NH_3})^2}{(p_{H_2})^3}$$

where $P_{N_2}^*$ is the fictitious pressure that gives the equivalent N_2-adsorption. If this "pressure" or fugacity is put into the adsorption isotherm and then Θ is eliminated from the rate equation the final equation becomes

$$r = k_1 p_{N_2} \left[\frac{(p_{H_2})^3}{(p_{NH_3})^2} \right]^\alpha - k_2 \left[\frac{(p_{NH_3})^2}{(p_{H_2})^3} \right]^{1-\alpha}$$

Later Temkin [21] showed that the same expression could be derived with the Freundlich isotherm which has an exponential decrease of the heat of adsorption with coverage and Boudart has demonstrated, as mentioned, that the Temkin equation could be derived with a pure Langmuir-Hinshelwood reasoning.

With the formal Hougen-Watson writing this derivation is simply done and if the slow step is assumed to be $N_2 + 2I = 2$ N-1 the rate equations becomes

$$r = \frac{k_1 L^2 \left[p_{N_2} (p_{H_2})^3 - (p_{NH_3})^2 / K \right]}{\left((p_{H_2})^{1.5} + K_N^{0.5} \, p_{NH_3} \right)^2}$$

With the approximation $kx/(1 + kx) \approx ax^{1-a}$ and with $x = K_N^{0.5}(p_{NH_3})/(p_{H_2})^{1.5}$ the equation above is transformed into the Temkin equation.

The different ways of deriving the Temkin rate equation have shown that rate equations seem to be quite insensible to the choice of adsorption isotherm. The exponential form of the rate equations may be easier to fit to the experimental data but the Langmuir form has the advantage of covering the whole pressure range. The Langmuir expression above shows for instance the limiting rates for high p_{H_2} and low p_{NH_3} and the reverse, to be $r = k \, p_{N_2}$ and $-r = k$, which has been experimentally observed.

In Table 1 some experimentally determined rate equations have been grouped together with their equivalent Langmuir or Temkin expressions. A star marks out the form in which the equation was presented in the literature. The equations in the table all show, when properly rewritten, how the factor $1/(P_1^a + K_1 P_2^b)$ in the Langmuir expressions is equivalent to $1/[(P_1^a)^n (P_2^b)^{1-n}]$. This last expression is similar in form to the "inhomogeneity factor" $F = [\Theta^n (1-\Theta)^{1-n}]$ which de Bruijn [20,24] derived from the Temkin ammonia-equation, assuming an arbitrary distribution of active centers. In fact, $1/F$ is exactly the factor which transforms, without mathematical approximations, a Langmuir expression ("ideal surface") to an exponent expression of the Temkin type ("inhomogeneous surface").

THE RELATION BETWEEN THE FORWARD AND BACKWARD REACTION RATES

The rate of a reaction can be written as the difference between the forward rate r_f and the backward rate r_b

$$r = r_f - r_b = k_f F_f - k_b F_b$$

where k_f and k_b are rate constants and F_f and F_b are algebraic expressions of the reactants and products A,B, ... and R,S, ... At equilibrium $r = 0$ and

$$\frac{F_b}{F_f} = \frac{k_f}{k_b} = f(T)$$

where k_f/k_b is a constant only determined by temperature. Usually this constant is put equal to the equilibrium constant of the reaction

Table 1. Comparison of rate equations.

r_T = exponential Temkin-form r_L = Langmuir-form

1. Reaction: $3\ H_2 + N_2 = 2\ NH_3$

* $$r_T = k_1 P_{N_2} \left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^n - k_2 \left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{1-n}\qquad\qquad n = \tfrac{1}{2}\qquad(20)$$

$$r_T = \left[\frac{1}{(P_{H_2}^3)^{1-n}(P_{NH_3}^2)^n}\right] k\ (P_{N_2}\ P_{H_2}^3 - P_{NH_3}^2/K)$$

$$r_L = \left[\frac{1}{P_{H_2}^3 + K_N\ P_{NH_3}^2}\right] k\ (P_{N_2}\ P_{H_2}^3 - P_{NH_3}^2/K);\ \ N_2\ \text{not dissociated}$$

$$r_L = \left[\frac{1}{(P_{H_2}^{1.5} + K_N^{0.5} P_{NH_3})^2}\right] k\ (P_{N_2}\ P_{H_2}^3 - P_{NH_3}^2/K);\ \ N_2\ \text{dissociated}$$

2. Reaction: $2\ SO_2 + O_2 = 2\ SO_3$

* $$r_T = k_1\ P_{O_2}\left(\frac{P_{SO_2}}{P_{SO_3}}\right)^{2n} - k_2\left(\frac{P_{SO_3}}{P_{SO_2}}\right)^{2(1-n)}\qquad \begin{matrix}V_2O_5-\text{cat: } n = \tfrac{1}{4}\\ Fe_2O_3-\text{cat: } n = \tfrac{3}{4}\end{matrix}\qquad\begin{matrix}(22)\\(23)\end{matrix}$$

$$r_T = \left[\frac{1}{(P_{SO_2}^2)^{1-n}(P_{SO_3}^2)^n}\right] k\ (P_{O_2}\ P_{SO_2}^2 - P_{SO_3}^2/K)$$

$$r_L = \left[\frac{1}{P_{SO_2}^2 + K_O\ P_{SO_3}^2}\right] k\ (P_{O_2}\ P_{SO_2}^2 - P_{SO_3}^2/K);\ \ O_2\ \text{not dissociated}$$

$$r_L = \left[\frac{1}{(P_{SO_2} + K_O^{0.5}\ P_{SO_3})^2}\right] k\ (P_{O_2}\ P_{SO_2}^2 - P_{SO_3}^2/K);\ \ O_2\ \text{dissociated}$$

* $$r_T = k_1\ P_{SO_2}\left(\frac{P_{O_2}^{0.5}}{P_{SO_3}}\right)^n - k_2\left(\frac{P_{SO_3}}{P_{O_2}^{0.5}}\right)^{1-n}\qquad Pt-\text{cat: } n = 1/2\qquad(23)$$

$$r_T = \left[\frac{1}{(P_{O_2}^{0.5})^{1-n}(P_{SO_3})^n}\right] k\ (P_{SO_2}\ P_{O_2}^{0.5} - P_{SO_3}/K)$$

$$r_L = \left[\frac{1}{P_{O_2}^{0.5} + K_S\ P_{SO_3}}\right] k\ (P_{SO_2}\ P_{O_2}^{0.5} - P_{SO_3}/K)$$

3. Reaction: $CO + H_2O = CO_2 + H_2$

* $$r_T = k_1 P_{CO}\left(\frac{P_{H_2O}}{P_{H_2}}\right)^n - k_2\ P_{CO_2}\left(\frac{P_{H_2}}{P_{H_2O}}\right)^{1-n}\qquad\qquad\qquad(18)$$

$$r_T = \left[\frac{1}{(P_{H_2})^n (P_{H_2O})^{1-n}}\right] k\ (P_{CO}\ P_{H_2O} - P_{CO_2}\ P_{H_2}/K)$$

$$r_L = \left[\frac{1}{P_{H_2} + K_O\ P_{H_2O}}\right] k\ (P_{CO}\ P_{H_2O} - P_{CO_2}\ P_{H_2}/K)$$

* $$r_L = \left[\frac{1}{P_{CO_2} + K_{CO}\ P_{H_2O}}\right] k\ (P_{CO}\ P_{H_2O} - P_{CO_2}\ P_{H_2}/K)\qquad(19)$$

$$r_T = \left[\frac{1}{(P_{CO_2})^n (P_{H_2O})^{1-n}}\right] k\ (P_{CO}\ P_{H_2O} - P_{CO_2}\ P_{H_2}/K)$$

$K_c = (R)^r(S)^s/(A)^a(B)^b$. Manes, Hofer and Weller [25] and Denbigh and Prince [26] have shown that this is not a necessary condition but that all thermodynamic conditions are fulfilled if only

$$\frac{k_f}{k_b} = f(T) = (K_c)^z \quad \text{and} \quad z > 0$$

Very often $z = 1$, which gives the classical relation $k_f/k_b = K_c$. Horiuti developed in 1939 the "stoichiometric number" which is defined as the coefficient with which the stoichiometric formula of every reaction step has to be multiplied to give the wanted coefficients in the stoichiometric formula of the total reaction. The stoichiometric number ν_r of the slowest, rate determining step has been shown by Horiuti [27,28] to be identical with $1/z$, and therefore

$$\frac{k_f}{k_b} = (K_c)^{\ 1/\nu_r}$$

The relation between the algebraic expressions for the forward and the backward reaction rate can now be written

$$\frac{F_b}{F_f} = \frac{k_f}{k_b} = (K_c)^{\ 1/\nu_r} = \left[\frac{(R)^r(S)^s}{(A)^a(B)^b} \right]^{1/\nu_r}$$

or

$$F_b = F_f \left[\frac{(R)^r(S)^s}{(A)^a(B)^b} \right]^{1/\nu_r}$$

The value of ν_r, the stoichiometric number of the rate determining step, is however not known. A reaction step must be assumed to be a reaction between whole particles — molecules or atoms — and therefore ν_r or $1/\nu_r$ must be an integral number. If different values of ν_r are inserted in the last equation above, different expressions for the backward rate will be obtained. Denbigh and Prince [26] found for instance in an experimental investigation $z = 1/\nu_r = 1/4$ in contrast to the expected classical $z = 1/\nu_r = 1$. The value of z is restricted as total reactions with high stoichiometric coefficients are seldom which is due to the fact that primary reactions between more than three particles are highly inprobable. The stoichiometric number is therefore assumed to vary between $1/4$ and 4.

It may be that some more restrictions on the stoichiometric number ν_r can be deduced in each investigated case and that reasoning in line with Christiansens [1] theory of sequences could be applied. The final determination must however, be made experimentally. If both F_f and F_b are determined it should be possible to calculate ν_r and from that obtain information useful for the determination of the rate determining step. Finally it can be mentioned that a relation exists, near equilibrium, between the free energy of the total reaction, the forward rate, the total rate and the stoichiometric number

$$\nu_r = (r_f/r) \, \Delta G/RT$$

which in special cases can be used for the determination of ν_r.

THE EXPERIMENTAL DESIGN OF KINETIC INVESTIGATIONS

It was pointed out in the introduction that even relatively modern kinetic investigations have a tendency of using hidden parameters and it is astonishing how limited the value often is of even large experimental series described in the literature on kinetics of reactions based on heterogeneous catalysis.

Some of the most often occurring factors which diminish the value of experimental data are

1. Too many variables such as contact-time, partial pressure and temperature have been varied at the same time so that only a few data points are unambigously showing the influence of one single variable.

2. The partial pressures have been varied only in narrow ranges of technical interest. A recalculation of the used pressures to mole-fractions will show this very clearly.

3. The contact-time has not been defined clearly.

4. The experiment has been designed so that too many temperatures have been investigated with too few data points for every temperature.

5. The absolute accuracy of analysis has been low.

6. Diffusion effects have been neglected or measured at low temperatures where the reaction rate has not its maximum value. Sometimes diffusion calculations are based on unsafe assumptions.

7. Different catalysts and different particle dimensions have been used without measuring the pore-diffusion effects.

8. The temperature distribution in the catalyst bed has not been measured during the reaction.

9. The catalyst has not been described in detail, has been undefined and chemical changes, ageing, and weight losses have been neglected.

10. The possibility of exchanging experimental data with calculated data has been overvalued.

The pronounced technical character of many investigations is naturally an explanation of the occurrence of some of these factors. A more careful experimental design would, however, without any marked increase in the amount of work, give experimental data of a much more general value. If a kind of standard procedure could be accepted for technical investigations some of the confusion in the literature would be eliminated and comparison of the literature data would be simpler.

With these views in mind a standard experimental design will be roughly outlined.

Apparatus

On the assumption that the analysis is accurate enough to permit the detection of small conversions a differential reactor should be used. For preliminary measurements integral-reactor measurements should also be possible. The constancy of the temperature must be better than $\pm$ 5°C at 500°C and it must be possible to measure the temperature all along the catalyst bed. The flow-meters — one for each gascomponent and one for the inert dilution gas — should have an absolute accuracy of better than 1 %. This can practically be obtained with the general calibration method for capillary flow-meters described by Ergun [29]; cf. also Benton [30]. If the total pressure of the system is held constant by means of a valve in the exhaust line, the flow measurements are further simplified.

Nomenclature

The reaction rate r should always be expressed as mass of converted material per unit mass of catalyst and unit time, *e.g.* (mole)/(g catalyst)(min). The mass of catalyst W should be expressed in (g). The area of the catalyst is often expressed in square-meters per g by the B.E.T. standard method. The gas feed F is expressed in mass per unit time, *e.g.* (mole)/(min). The contact-time W/F is then independand of the temperature of the reactor and is exactly defined as for instance (g catalyst)(min)/(mole F). The conversion x is expressed as converted mass of initial feed F_o, *e.g.* (mole converted F_O)/(mole F_O). When integral-reactor data are represented by the function $x = f(W/F)$, the conversion x must always be calculated on the same feed F with which the contact-time is calculated. If for instance F is the total feed of gas then x must be calculated on the total feed F, etc.

Program for experimental runs

1. Diffusion effects. The effect of the external diffusion is determined at the highest temperature used in the investigation (highest rate) by the relation between the conversion x and the feed F at constant W/F. Above a certain limiting gas velocity F_D the conversion x is constant. A simple approximation formula is given by Wheeler [31].

The internal diffusion (pore-diffusion) is determined by measuring x at constant W/F and varying the diameter of the catalyst particles d. Under a certain diameter d_D the conversion x is constant. Calculating formulas are given by Wheelei [31] and recently a general formula by Weisz [32].

2. Preliminary data. Integral-reactor data with $F \geq F_D$ and $d \leq d_D$ are taken for different contact-times W/F and the function $x = f(W/F)$ is obtained. This function can be considered as a graphical form of the rate equation and can be used for preliminary calculations. The initial feed-gas-mixture should be varied widely for instance in the proportions 1:4, 1:1 and 4:1.

3. Initial-rate data with variation of one partial pressure. Initial-rate data are produced in the following way: The total pressure and all partial pressures except one (and the inert gas) are kept constant. One partial pressure is varied from very low to very high values while the whole gas-mixture always is kept far away from equilibrium values to avoid the influence of the reverse reaction. As the conversion x is kept low the reaction rate is $r = x(F/W)$ where $x \leq 5 \%$ of the equilibrium conversion. All reactants and products are studied in this way and the experimental data are graphically represented. Inspection of the curves with the help of the Langmuir-Hinshelwood reasoning gives hints to possible mechanisms and these can be further investigated by experiments with pressures chosen in a crucial way. For instance the mole-fraction method of Hougen and Yang [7].

4. Tests with the established rate equation. A final rate equation with its mechanism — for derivations the Hougen-Watson formalism can be used with advantage — is established and the expressions for the formal and backward reaction are examined from a thermodynamic point of view by means of Horiuti's theorem for stoichiometric numbers. A fit to the integral-reactor curves is made and constants are evaluated by graphical methods.

5. Influence of temperature. After the establishment of the rate equation measurements at two relatively different temperatures are started. Only a limited number of runs are necessary as the rate equation is known. Activation energies are calculated from the temperature variation of the constants. Bends in the Arrhenius lines have been discussed by Christiansen[1]. A bend concave upward or downward shows that two parallell or two series reactions are involved.

*6. Investigations of other catalysts.* If the purpose of the investigation was not only the establishment of the rate equation but also information about the catalyst, the change in mechanism when promotors are added etc., the investigation can with advantage be carried on with the initial-rate method. Determination of the activation energy can give informations concerning the influence of additives and of different methods of treatment. A detailed program on catalyst-testing has recently been given by Dowden and Bridger [33].

Finally experiments in static systems can sometimes complement the outlined course of the investigations, as for instance adsorption measurements of the different gas-components. Reference is again made to the work of Gadsby, Hinshelwood and Sykes [2] and subsequent works [3-5].

The watergas-shift reaction

As an example of how the proposed experimental procedure can be applied some results will be presented here of an investigation of the watergas-shift reaction [34].

The rate of the reaction

$$CO + H_2O = CO_2 + H_2$$
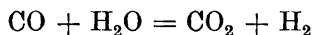
was studied in the presence of an iron-oxide catalyst. The diffusion- and pore-diffusion effects were measured and the allowed minimum gas velocity and maximum particle size was determined. With an integral reactor preliminary data were produced but partly due to the ageing of the catalyst a Hougen-Watson treatment to determine the rate equation was not successful.

Then the initial-rate method was applied and the difficulties of ageing gave no trouble as now the general form of the curves, rather than their exact slope, is the important factor for the evaluation. The experimental rate expressions for the different varied partial pressures were then united in one rate equation. A comparison with the integral-reactor data was made and constants were determined. Some of the measurements are presented in Fig. 2 which shows the variation of the forward rate when different gas-components are varied in pressure. From Fig. 2 c it can be seen that even very small amounts of CO_2 have a strong inhibiting effect. If the experimental curve I in Fig. 2 a is corrected for the small CO_2-amount produced at the low conversion used, the corrected curve II shows that the rate is directly proportional to p_{CO}.

The other curves indicate that H_2O and CO_2 are strongly adsorbed and that H_2 does not take part in the reaction. The experimental rates can be grouped together to the form

$$r_f = f\left[(p_{CO}), \left(\frac{p_{H_2O}}{b + K_1 p_{H_2O}} \right), \left(\frac{1}{c + K_2 p_{CO_2}} \right), (p_{H_2})^0 \right]$$
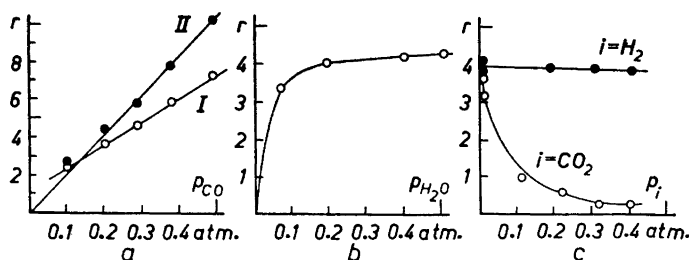
Fig. 2. The variation of the forward rate of the watergas-shift reaction when partial pressures of only one reactant or product are varied. Iron-oxide catalyst. Temperature 390°C. Pressures in atm. Rates in $(10^{-4}$ mole) / (g catalyst) (min). In Fig. 2 a the curve II represents the values of curve I, corrected for CO_2-inhibition.

By closer inspection of the data this is transformed into the rate equation for the forward reaction

$$r_f = k \frac{p_{CO} p_{H_2O}}{p_{CO_2} + K_B p_{H_2O}} \approx k \; p_{CO} \left[\frac{p_{H_2O}}{p_{CO_2}} \right]^n$$

In this rate equation the influence of each gas-component has been unambigously determined and the experimental approach has eliminated such parameters as diffusion, particle size and temperature variations. Variables as partial pressures and contact-times have been used directly for the rate determination and are not parameters.

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