tion changes but slowly with hydrogen pressure from 9 to 620 mm.; (3) sorption is slow.

There does not appear to be a good correlation of hydrogen sorption with the surface area of the aluminas or with their known amounts of chemical impurities. The apparent sorption of hydrogen is increased temporarily by exposure of the alumina to air or oxygen before measurement, by washing with water or by heating from 750 to 900° in vacuum. Prolonged evacuation of the alumina at high temperature is necessary to remove previously sorbed hydrogen from it. The sorption values indicate that less than one per cent. of the available alumina area is covered with hydrogen at equilibrium.

Summary

The sorption of hydrogen on various samples of alumina has been measured from 400 to 900° and from 9 to 620 mm. Sorption is in the range 0.05 to 0.2 ml. STP/g., increases with decreasing temperature, and increases proportional to the fourth root of pressure. The results reported in this paper are roughly consistent with those of Taylor.[1] Sorption equilibrium is slow and difficult to reproduce and there is evidence of an irreversible hydrogen reaction on alumina. The samples tested have sorption in the same range in spite of large differences in their surface areas and impurity contents.

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[Contribution from the Central Experiment Station, Bureau of Mines]

Generalized Form of the Reaction-Rate Law for Homogeneous Reactions[1a]

By Stuart R. Brinkley, Jr.,[1b] and Sol Weller[1b]

The classical equations of reaction kinetics, relating the rate of reaction to the concentrations of the reacting substances, are correctly applied to static systems maintained at constant volume and to flowing systems in which no volume change occurs during the reaction. A large number of reactions have been studied in flowing systems, in which the pressure is essentially constant but in which the volume changes. There does not appear to be substantial agreement as to the proper form of rate law applying to such systems. Benton[1c] has considered several special cases, and Hulburt[2] has recently presented a discussion of reaction kinetics in flow systems based upon the hydrodynamic equations for reaction mixtures which includes a treatment of first and second order reactions. It is not, however, obvious from the discussion that the proper form of rate law has been employed. In the present communication, the appropriate rate equation for a flowing system is derived, it being assumed that the reaction is homogeneous.

The general hydrodynamic equations for reacting fluids have been given by Bateman[3] and Eckart.[4] The present discussion is based upon the equation for the transport of each kind of substance, which may be written in the form

$$\rho \frac{\mathrm{d}m_k}{\mathrm{d}t} = \rho\Gamma_k + \nabla \cdot D_k \nabla \rho m_k \qquad (1)$$

where ρ is the mean density of the mixture, m_k the concentration of the k-th constitutent of the mixture in moles per unit weight of mixture, t the time, Γ_k the rate of production of the k-th constituent in moles per unit weight of mixture, and D_k the diffusivity of the k-th constituent in the mixture. The Euler total time derivative $\mathrm{d}/\mathrm{d}t$ follows the fluid and refers to changes in an elementary volume which moves with the fluid and always contains the same molecules (either in reacted or unreacted form). The Euler total time derivative is related to Euler and Lagrange partial derivatives by

$$\frac{\mathrm{d}}{\mathrm{d}t} = \left(\frac{\partial}{\partial t}\right)_{\mathbf{R}} + \mathbf{u}\cdot\nabla = \left(\frac{\partial}{\partial t}\right)_{\mathbf{R}_0} \qquad (2)$$

where $\mathbf{R} = \mathbf{R}\ (\mathbf{R}_0, t)$ is the position vector at time t of the elementary volume which was at $\mathbf{R}_0$ at a reference time t_0, and $\mathbf{u}$ is the (vector) velocity of the fluid.[5] If the reactor is isothermal, the form of the function $\mathbf{R}\ (\mathbf{R}_0, t)$ is obtained from a consideration of the fundamental hydrodynamic equations for transport of total mass and momentum, and it is always possible, at least in principle, to find this solution of the purely hydrodynamic aspect of the problem. It follows from equation (2) that equation (1) can be integrated in a manner exactly analogous to that for the static case, after the form of the source function Γ_k is explicitly given, provided only that the integration be performed along a path of constant Lagrange coördinate $\mathbf{R}_0$. The limits of integration for the time will be the time t_1 at which a selected element of volume enters the reactor and the time t_2 at which the

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(1c) Benton, This Journal, **53**, 2984 (1931).

(2) Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944).

(3) Bateman, *Proc. Natl. Acad. Sci.*, **25**, 388 (1939).

(4) Eckart, *Phys. Rev.*, **58**, 269 (1940).

(5) $\mathbf{R}_0$, the Euler coördinate of the element of volume at the reference time t_0, is the Lagrange coördinate of the element of volume. Specification of its value can be considered to provide the element with a label which it carries throughout its subsequent history, and a restriction to constant Lagrange coördinate provides a notation indicating that differentiation or integration subject to this restriction is to be performed following the fluid in the same sense with which the Euler total time derivative follows the fluid.

element of volume leaves the reactor; the difference, $t_2 - t_1$, is the contact time for the reacting system. The relation between the contact time and the operating variable, space velocity, has been discussed elsewhere.[6]

The transport of the k-th constituent by diffusion may usually be neglected in comparison to its transport by the mean flow of the system, and in this case

$$\mathrm{d}m_k/\mathrm{d}t = \Gamma_k \tag{3}$$

In view of the foregoing discussion, Γ_k may be considered to be simply the rate of production of the k-th constituent in moles per unit weight of mixture, the fact that the fluid is in motion being irrelevant since the point of reference may be considered to move with the fluid. The form of Γ_k for flowing systems may, therefore, be obtained by consideration of the reaction-rate law for static systems.

The law of mass action was first formulated in 1867 by Guldberg and Waage[7] as follows: The rate of a chemical reaction is proportional to the "active masses" of the reacting substances present. For ideal systems,[8] the "active mass" of a constituent is taken to be the volume concentration of the constituent, raised to a power equal to the coefficient to the symbol of that constituent in the equation for the reaction. Thus, for the forward reaction in

$$\Sigma_i a_i A_i \rightleftarrows \Sigma_j b_j B_j$$

one writes[9]

$$\text{rate} = k\Pi_i c_i^{a_i} \tag{4}$$

where A_i represents the symbol of the i-th reactant and c_i is the concentration of that reactant in moles per unit volume of mixture. The correctness of the form of this rate equation is verified by consideration of the system at equilibrium, it being known from thermodynamics that $\Pi_j c_j^{b_j}/\Pi_i c_i^{a_i}$ = constant for ideal systems when the rates of the forward and backward reactions are equal. If volume change accompanies the reaction, this quotient is constant and independent of the volume only if the rate equations for forward and backward reactions is of the form (4) in which the concentrations are expressed on a volume basis.

The form of the right side of equation (4) is valid for all reactions in ideal systems, whether at constant volume or not. The problem remains of determining for the general case the correct manner in which the rate of reaction is to be expressed. In the case of reactions at constant volume, the rate may be measured by either of the two quantities, $-(\partial c_k/\partial t)_v$ or $-(\partial m_k/\partial t)_v$, where the k-th reactant has been chosen as a reference constituent, since the two quantities differ only by a constant factor, the density, which may be incorporated in the specific rate constant. Therefore, at constant volume, the rate law may be written as

$$-\left(\frac{\partial c_k}{\partial t}\right)_v = f(\cdots, c_i, \cdots) \tag{5}$$

where the form of the function f for an elementary reaction is determined by the reaction under consideration in the manner indicated by equation (4). If the over-all rate of a complex reaction is under consideration, the function f may always be written in the form, $f(\cdots, c_i, \cdots) = k[\Pi_i c_i^{a_i}]/g(\cdots, c_i, \cdots, c_j, \cdots)$, rather than as indicated by equation (4).[9] The validity of the subsequent treatment does not depend on the algebraic form of the right side of equation (5).

In a system in which the volume changes with time, the volume concentration of any constituent may be considered to be a function of time depending explicitly on the volume, $c_k = c_k[v(t), t]$, and the total rate of change of the volume concentration with respect to time is given by

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \left(\frac{\partial c_k}{\partial t}\right)_v + \left(\frac{\partial c_k}{\partial v}\right)_t \frac{\mathrm{d}v}{\mathrm{d}t} \tag{6}$$

Introducing the density, $\rho = 1/v$, the concentrations on the weight basis, $m_i = c_i/\rho$, and employing equation (5) to evaluate $(\partial c_k/\partial t)_v$, equation (6) becomes

$$\rho \frac{\mathrm{d}m_k}{\mathrm{d}t} = -f(\cdots, \rho m_i, \cdots) \tag{7}$$

Equation (7) is a more general form of the rate law than equation (5), since it is not restricted to systems at constant volume. It should be noted that the density in the general case depends implicitly on the time through its explicit dependence on the composition of the system. Comparing equations (3) and (7), it is apparent that the source function Γ_k of the rate equation for the flowing system is given by

$$\Gamma_k = -\frac{1}{\rho} f(\cdots, \rho m_i, \cdots) \tag{8}$$

where the function f is obtained from the form of the rate law for the reaction under consideration in a static system at constant volume. We note that the rate law for the flowing system is exactly analogous to the general form for static systems, equation (7), the time derivative being inter-

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(6) Brinkley, *Ind. Eng. Chem.*, to be published.

(7) Guldberg and Waage, "Études sur les affinités chimiques," Christiania, 1867.

(8) The designation "ideal system" will be used here to mean a system for which the activity coefficient of each constituent is unity at all times, and the discussion which follows is intended to apply only to such systems. This is done to avoid the current uncertainty regarding the use of concentration or of activity to represent the "active mass" of a constituent; a typical discussion of this problem is that by LaMer, *Chem. Rev.*, **10**, 179, (1932).

(9) Gadsby, Hinshelwood and Sykes (*Proc. Roy. Soc.* (*London*), **187**, 129 (1946)) have pointed out that if the over-all reaction involves more than one elementary reaction, the over-all rates in the forward and back directions may in general be given by

$$\text{rate}_f = k_f \frac{\Pi_i c_i^{a_i}}{g(\cdots, c_i, \cdots, c_j, \cdots)} \text{ and}$$

$$\text{rate}_b = k_b \frac{\Pi_j c_j^{b_j}}{g(\cdots, c_i, \cdots, c_j, \cdots)}$$

respectively, where the same functions $g(\cdots, c_i, \cdots, c_j, \cdots)$ appears in both expressions. Equation (4) is valid, however, for each elementary intermediate step in a complex reaction.

preted, in the flowing case, as the Euler total time derivative which follows the fluid. It is easy to show that this equation is not restricted to reactors operating with negligible pressure drop, since the density may be considered to depend explicitly on both the composition and the pressure, each of which depend explicitly on the time of contact.

These considerations are in agreement with the expressions which were obtained by Benton[1] with a less general argument for the special cases of first- and second-order reactions at constant pressure, and they confirm the form of rate law that was employed, without supporting argument, by Hulbert.[2]

The hydrodynamic rate law, equations (3) and (8), may be written in various forms for special cases. For example, if the system has attained the steady state, it is sometimes convenient to employ position as independent variable instead of time of contact by means of the substitution (*cf.* equation (2)) $d/dt = \mathbf{u}\cdot\nabla$.

If the reactor cannot be considered to be isothermal, the solution of the hydrodynamic problem must include consideration of the equation for energy transport, and the rate constant becomes a function of temperature, which may be considered to depend explicitly upon the time of contact (or upon position).

At low velocities of flow, diffusion may be of sufficient importance to require consideration of equation (1) instead of its approximate form, equation (3).

It has been assumed that the reaction is homogeneous. A more elaborate analysis is required if surface reactions or diffusion to a surface are rate controlling.[1,10,11]

Summary

1. A reaction-rate law, which is not restricted to either constant pressure or constant volume, is obtained for homogeneous, isothermal reactions in ideal systems.

2. It is shown that this expression is applicable to flowing systems with negligible diffusion if the time derivative is interpreted as the Euler total time derivative which follows the fluid.

3. Mention is made of the modifications required for the consideration of systems which are non-isothermal or in which diffusion currents are not negligible.

(10) Benton, *Ind. Eng. Chem.*, **19**, 494 (1927).

(11) Hulburt, *ibid.*, **37**, 1063 (1945).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Stability and Light Absorption of the Complex Ion $FeSCN^{++}$

BY HENRY S. FRANK AND ROBERT L. OSWALT

Introduction

Møller[1] was apparently the first to publish evidence that when Fe^{+++} and SCN^- are mixed at high dilution the principal colored substance formed is $FeSCN^{++}$, but this conclusion was also reached independently by Bent and French,[2] Edmonds and Birnbaum[3] and by at least one other group[4] as well. In each case an estimate was made of the value of K_1 for the reaction

$$Fe^{+++} + SCN^- = FeSCN^{++} \qquad (1)$$

but these results are not equally susceptible of straight-forward interpretation. Rabinowitch and Stockmayer[5] have shown that several complexes of Fe^{+++} and Cl^- exist, and have found K for

$$Fe^{+++} + Cl^- = FeCl^{++} \qquad (2)$$

to have a value close to 4.2 in perchlorate solutions at an ionic strength of 1.0. They have also shown that when (Cl^-) is greater than a few hundredths molal higher chloride complexes cannot be neglected. The fact, therefore, that Møller and Bent and French worked in chloride solutions and either took no account of ferric chloride complexes or treated them in ways incompatible with Rabinowitch and Stockmayer's figures makes it impossible to use their values of K_1 without further discussion (see below).

The Edmonds and Birnbaum value of K_1, on the other hand, should be usable as it stands, for they worked in perchlorate solutions, with perchloric acid at about 1.0 M to repress hydrolysis and keep the ionic strength constant at unity and there seems to be no evidence either for the formation of complexes between Fe^{+++} and ClO_4^- or for weakness of thiocyanic acid.[6] Their value of $1/K_1$ for room temperature is 0.0079 ± 0.0006. They do not report the wave length or range of wave lengths used in their experiments, and give

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(1) Max Møller, "Studies on Aqueous Solutions of Iron Thiocyanates," Copenhagen, Dana Bogtrykkeri, 1937.

(2) H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

(3) S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

(4) Reuben E. Wood and Miss Tsao Hang-Sang worked on this problem with one of us (H. S. F.) at Lingnan University in 1935 and 1936. The former made measurements with a Duboscq colorimeter which established the 1-1 composition of the first complex. Miss Tsao subsequently constructed a photometer using balanced photronic cells and studied the equilibrium in sulfate solutions using 2.0 M sulfuric acid to repress hydrolysis and provide sensibly constant ionic strength. She obtained a value for K_1 of 100 ± 10.

(5) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(6) A rough test of the latter point was made by adding methyl violet indicator to 10-cc. portions of 1.0 M potassium chloride and 1.0 M potassium thiocyanate and slowly adding 6 N hydrochloric acid to each. For equal additions of acid the colors of the two solutions were practically indistinguishable all the way from clear violet to clear yellow.