TABLE 1. DIFFUSION BEHAVIOR* OF THE SYSTEM

WATER (0)-GLYCINE (1)-POTASSIUM CHLORIDE (2)

c_0	moles/liter	54.44	54.35	53.95	53.94	53.74	53.33
c_1		0.25	0.25	0.25	0.50	0.50	0.50
c_2		0.125	0.25	0.50	0.125	0.25	0.50
$(L_{11})_0$	$\times 10^8\, RT$ moles²/cm., sec.	0.265	0.265	0.264	0.525	0.524	0.522
$(L_{22})_0$		0.123	0.249	0.501	0.119	0.241	0.482
$(L_{12})_0$		0.003_4	0.004_7	0.009_4	0.005_8	0.008_2	0.017
D_{10}	$\times 10^5$ sq. cm.²/sec.	1.074	1.080	1.096	1.061	1.064	1.081
D_{20}		0.988	1.004	1.019	0.961	0.973	0.993
D_{12}		0.17	0.27	0.27	0.20	0.27	0.27

* The D_{ij} are calculated from the c_i and $(L_{ij})_0$ of reference *6*. The significance of even the first figure of the $(L_{12})_0$ is doubtful (see reference *6*).

$$D_{02} = (x_0 DRT/c)/[x_2(L_{11})_0 - x_1(L_{12})_0] \quad (18)$$

$$D_{12} = (DRT/c)/(L_{12})_0 \quad (19)$$

where $D = (L_{11})_0 (L_{22})_0 - (L_{12})_0^2$.

The results of Woolf, Miller, and Gosting are summarized in Table 1, and at the bottom of the table are shown the D_{ij} as calculated from Equations (17) through (19). It can be seen that these multicomponent diffusion coefficients are reasonably concentration independent, especially if the large experimental uncertainty of the cross term D_{12} is taken into account. It is also apparent that D_{12} is very much lower than D_{10} or D_{20}. Part of this difference may result from the relatively low molecular weight of water, but this explanation does not seem sufficient. It appears that this unexpectedly high frictional resistance may result from the electrostatic charges on potassium chloride and the glycine, which latter is almost entirely in the zwitterion form. This would be an interesting possibility to investigate further. One finds then that the D_{ij} are doubly useful in this system, first from a practical point of view, because they are much less concentration dependent than the $(L_{ij})_0$ most commonly used at present, and second because they provide a method for further and more fundamental investigation of the cross terms in the diffusion equation. Binary diffusion coefficients, based on concentration driving forces, are about 1.0 and 1.8 times 10^{-5} sq. cm./sec. respectively for glycine-water and potassium chloride-water under these conditions. The corresponding binary diffusivities based on free energy driving forces are nearly the same as the D_{10} and D_{20} of Table 1.

A few more examples of the usefulness of the D_{ij} could also be presented here, for example in explaining the behavior of the very interesting restrained quaternary system water-potassium-sodium-chlorine recently investigated by Dunlop and Gosting (*6*). Again the D_{ij} prove to be very weak functions of concentration.

Investigation of multicomponent diffusion in condensed systems is still in its infancy however, and the real test of the usefulness of the D_{ij} is still to come. The authors are now initiating an extensive series of such tests, both in true solutions and gels. Clearly one cannot expect to obtain very much information merely by such formal definitions as given above. It is hoped however that the definitions chosen here will facilitate estimation of the effects of solution properties on diffusional behavior.

NOTATION

a_i = thermodynamic activity of species i
c_i = molar concentration of species i
c = total molar density of solution $= \Sigma_i c_i$
F = Faraday's constant
g_i = body force per unit mass on species i
M_i = molecular weight of species i
N_i = molar flux of species i with respect to stationary coordinates
p = pressure
R = international gas constant
T = absolute temperature
$\tilde{V}_i$ = partial molal volume of species i
v_i = (observable) velocity of species i with respect to stationary co-ordinates
x_i = c_i/c = mole fraction of species i in the mixture,
α_{ij} = Onsager phenomenological coefficient, considered to be a system property
∇ = del, or nabla, operator
μ_i = chemical potential of species i
ν_i = change of species i, for example —1 for chlorine
ϕ = electrostatic potential

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Gas Absorption with Simultaneous Irreversible First-Order Reaction

II. Comparison of Results for the Film and Penetration Models

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Considered here is the absorption of a sparingly soluble reactive gas in an agitated tank, under such conditions that the gas may be assumed to undergo irreversible first-order reaction in the absorbing liquid. It is shown that the predicted effect of chemical reaction on gas absorption rate is very nearly equivalent for stagnant-film and

penetration models. From these results it appears that one may obtain adequate predictions of the effect of chemical reaction without detailed knowledge of the physical behavior of the gas and liquid in the tank.

To obtain precise expressions for the effect of chemical reaction on mass transfer rate one must normally assume a model for the physical system under consideration, for example a film, penetration, or boundary-layer model. All too frequently however it is difficult to find a model which gives a really satisfactory description of system behavior. It is therefore desirable, where possible, to develop approximate expressions capable of giving acceptable predictions of the effect of chemical reaction and which are not restricted to a single physical model. It was shown recently (*1*) that such a general expression could be obtained for gas absorption accompanied by fast second-order reaction. The purpose of the present paper is to show that the same can be done for gas absorption accompanied by irreversible first-order reaction. Consider specifically the pseudo steady state absorption of a sparingly soluble reactive gas into a gassed, agitated, tank (*2*, *3*). Such operations are of considerable importance and have been the subject of numerous previous analyses.

Consider specifically the penetration and stagnant-film models, for which the rate of absorption can be expressed by (2):

$$R = \frac{b}{\sinh b}\left(\cosh b - \frac{1}{\cosh b + b(V/A\delta)\sinh b}\right) \text{ (film)} \quad (1)$$

$$R = \left(\tau_0 + \frac{1}{2} - \frac{C_0}{C_i}\right)\frac{\sqrt{\pi}}{2}\frac{\operatorname{erf}\sqrt{\tau_0}}{\tau_0} + \frac{e^{-\tau_0}}{2} \text{ (penetration)} \quad (2)$$

with

$$\frac{C_0}{C_i} = \frac{\operatorname{erf}\sqrt{\tau_0} + \frac{1}{2}\left\{e^{\xi_0}\operatorname{erfc}\left(\frac{\xi_0}{2\sqrt{\tau_0}} + \sqrt{\tau_0}\right) - e^{-\xi_0}\operatorname{erfc}\left(\frac{\xi_0}{2\sqrt{\tau_0}} - \sqrt{\tau_0}\right)\right\}}{\xi_0[1 - e^{-\tau_0}\operatorname{erf}(\xi_0/2\sqrt{\tau_0})] + \sqrt{\tau_0}\, e^{-\tau_0}\,(2/\sqrt{\pi})[1 - \exp(-\xi_0^2/4\tau_0)]} \quad (3)$$

One can however use a more general pair of parameters to describe this system:

$$N_{sh} = k_L/S\,\mathfrak{D}_{Am} \quad (4)$$

$$K = \sqrt{k_1'''\,\mathfrak{D}_{Am}/k_L^2} \quad (5)$$

The first of these describes the effect of mass transfer resistance relative to system size and the second the relative importance of chemical reaction and physical absorption.

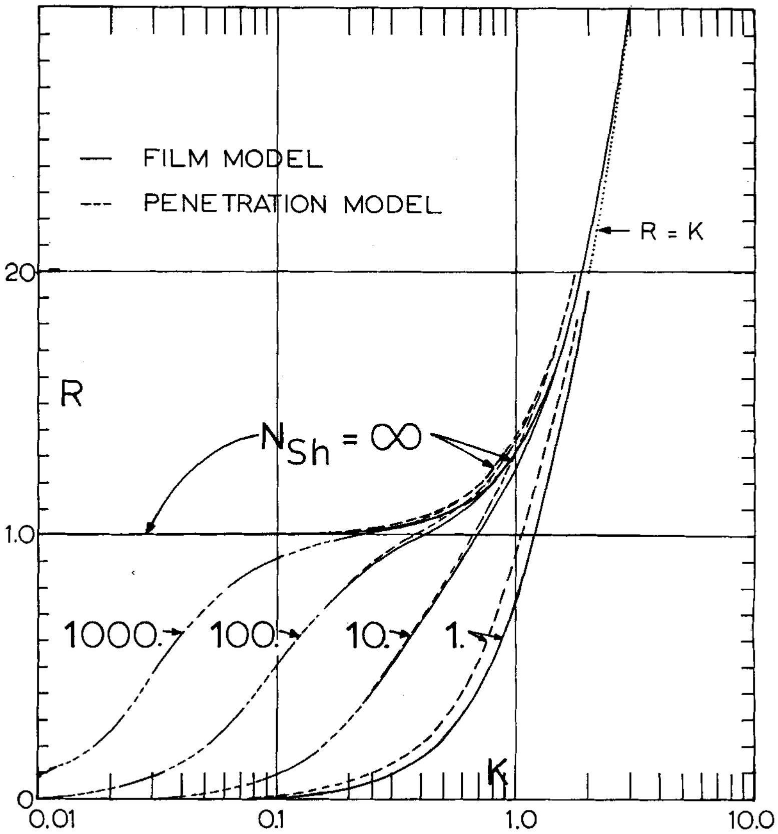

Fig. 1.

Making use of the assumed model behavior in each case, and of the definition of the mass transfer coefficient (4), one may write

$$V/A\delta = N_{sh} \quad (4a)$$

$$\xi_0/2\sqrt{\tau_0} = (\sqrt{\pi}/2)\,N_{sh} \quad (4b)$$

$$b = K \quad (5a)$$

$$\tau_0 = (4/\pi)\,K^2 \quad (5b)$$

Equations (1) through (3) can then be rewritten in terms of these new variables, and each of these new relations can be used to calculate $R(N_{sh}, K)$.

Some representative results of such calculations are shown in Figure 1. It can be seen on inspecting this figure that $R(N_{sh}, K)$ is very nearly the same for both models, even in the rather extreme limit of $N_{sh} = 1$ (entire liquid volume inside the film for the stagnant-film model). It can further be shown that the area shown in the figure is that for which disagreement between the two models is greatest. For both high and low values of K the two models give identical limiting expressions:

$$\mathop{\mathrm{Lim}}_{K}\{R(N_{sh}, K)\} = K \quad (6)$$

$$\mathop{\mathrm{Lim}}_{N_{sh}}\{R(N_{sh}, K)\} = N_{sh}K^2/(1 + N_{sh}K^2) \quad (7)$$

Roughly speaking Equation (7) is acceptable when K is less than about ¼ for all N_{sh} greater than 10.

One finds then that the effect of chemical reaction over most of the range of interest may be adequately represented by either of the sets of curves in Figure 1. By extension it seems reasonable that these results might give acceptable descriptions for other models as well and hence be of considerable practical value in predicting the gas-absorption behavior of the agitated tanks under consideration.

NOTATION

A = total interfacial area between gas and liquid in the tank, L^2

b = $(k_1'''\,\delta^2/\mathfrak{D}_{Am})^{1/2}$, dimensionless

$\mathfrak{D}_{Am}$ = effective average diffusion coefficient for the dissolving gas through the liquid in the tank, L^2/t

k_L = average mass transfer coefficient in the liquid phase, L/t

k_1''' = first-order reaction rate constant, t^{-1}

R = rate of gas absorption, divided by the corresponding rate in the absence of chemical reaction, and for zero concentration of dissolved gas in the tank liquid

$\overline{S}$ = specific surface of liquid in tank = A/V, L^{-1}

V = total volume of liquid in tank, L^3

δ = film thickness (film theory), L

τ_0 = $(4/\pi)\ \mathcal{D}_{Am}\ k_1'''/k_c^2$ (penetration theory), dimensionless

ξ_0 = $(k_1'''/\mathcal{D}_{Am})^{1/2}/\overline{S}$ (penetration theory), dimensionless

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Kinetics of Reduction of Ferrous Oxide with Hydrogen

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I have read with much interest the paper by Fienman and Drexler (*1*) in which the authors have postulated a scheme of reduction of ferrous oxide by molecular hydrogen at the metallic oxide-metal interface based on the general theory of noncatalytic heterogeneous reactions (2) with the added assumption that the transport processes offer negligible resistance to the overall reaction rate. This has led to the natural simplification that the reaction rate at the receding decomposition interface is considered to be a function of the reactant activity in the bulk gas stream rather than at the interface. While such a basis would be quite valid in cases where the dimensions and structure of the reducing particles and temperature of reduction would warrant the applicability of such a simplifying assumption, it would be desirable to incorporate the transport resistance in the rate equation so that it may be integrable for any general case. The recent paper by Walsh (3) has discussed a reduction scheme for iron oxides with hydrogen and carbon monoxide based on the assumption of rapid surface chemical reaction and controlled by counter diffusion (equimolal) of the gases. The recent investigation of the author (5) is concerned with the mechanism of thermal decomposition of calcium carbonate which also is based on a rapid surface reaction. It has been proven that under the conditions of experimentation the decomposition rate is entirely governed by the rate of heat transport to the decomposition interface, under quasisteady state conditions, to sustain the endothermic reaction. The simultaneous process of mass transfer concerns the unidirectional diffusion of carbon dioxide away from the interface and through the porous oxide layer. In a recent investigation (*4*) in the field of heterogeneous catalytic reactions it has been shown that the height of a reactor unit can be estimated with precision by splitting the transport resistance of the gas streams in terms of height of transfer units for both the reactants and products. It will be shown later that the rate equations derived for cases cited under investigations (3) and (5) have almost identical forms. This is to be expected, since the underlying assumption of a rapid surface reaction is the same in both the cases. It would therefore seem desirable to revise the mechanism of reduction of iron oxides by including the effect of transport processes in the general treatment.

Figure 1 represents a segment of a reacting sphere at some stage of reduction. The model used is identical with the one used in the earlier investigation (3). The decomposition plane is situated at a radial distance r from the center of the spherical particle. The bulk flow of the reducing gas introduces a boundary layer around the sphere which can be equated to a hypothetical film of thickness Z_g. The porous metallic layer of thickness $R - r$ has a structure which imparts certain physicochemical properties to the layer, like effective thermal conductivity k_e for the transport of heat and effective diffusivity D_e for the transport of mass inside the reacting sphere. The endothermic reaction at the interface is sustained by the transport of heat across the metallic layer, and the equivalent film and the simultaneous process of mass transfer involves equimolal counter diffusion in the system; hydrogen-water vapor and inerts or carbon monoxide-carbon dioxide-inerts. If the partial pressure of hydrogen at the reducing interface is p_i, that at the metal-film interface p, and that in the bulk p_o, under quasisteady state conditions the diffusional rate for hydrogen across the equivalent film may be equated with that across the metallic layers to provide the following equation for the interfacial partial pressure (5):

$$p_i = p_o - \frac{\alpha\rho R}{kg} \cdot r'^2 \cdot \left[1 + \frac{K_M(1 - r')}{r'} \right] \frac{dr'}{d\theta} \quad (1)$$

The rate of surface reaction at any time θ may be written as

$$-\rho R \frac{dr'}{d\theta} = k_r\ (p_i - p_{H_2O}/K) \quad (2)$$

Substituting for p_i from Equation (1), and rearranging one gets

$$-\frac{dr'}{d\theta} = \frac{k_r(p_o - p_{H_2O}/K)}{\rho \cdot R + \dfrac{k_r \cdot \alpha \cdot \rho \cdot R}{k_g} r'^2 \left[1 + \dfrac{K_M(1 - r')}{r'} \right]} \quad (3)$$

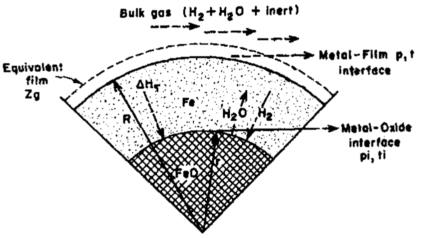

Fig. 1. Reduction scheme for system ferrous oxide + hydrogen ⇄ iron + water.