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

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

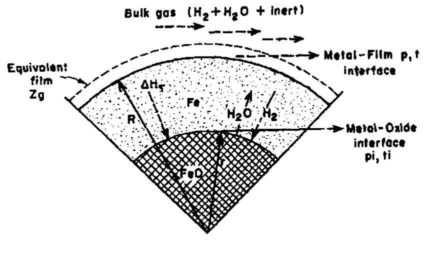

Fig. 1. Reduction scheme for system ferrous oxide + hydrogen ⇄ iron + water.

Equation (3) may be written as

$$-\frac{dS}{d\theta}=\frac{3QS^{2/3}(p_{H_2}-p_{H_2O}/K)}{d_o\cdot r_o+\frac{\alpha\cdot d_o\cdot r_o\cdot Q}{k_g}\cdot S^{2/3}\cdot\left[1+\frac{K_M(1-S^{1/3})}{S^{1/3}}\right]} \quad (4)$$

Dividing numerator and denominator by 3 $Q\cdot S^{2/3}$ one obtains

$$-\frac{ds}{d\theta}=\frac{(p_{H_2}-p_{H_2O}/K)}{\frac{d_o\cdot r_o}{3QS^{2/3}}+\frac{\alpha\cdot d_o\cdot r_o}{3k_g}\left[1+\frac{K_M(1-S^{1/3})}{S^{1/3}}\right]} \quad (5)$$

A comparison of Equations (5) and (12) appearing in the paper under discussion show that the second term in the denominator represents the combined transport resistance for the boundary layer and the porous metallic layer which is neglected for cases where the rate controlling step is the surface reaction. When one reverts to earlier symbols, Equation (3) may be integrated with limits $r' = 1$, $\theta = 0$; $r' = r'$, $\theta = \theta$:

$$\theta=\frac{\alpha\rho R}{k_g(p_o-p_{H_2O}/K)}\left[\frac{k_g(1-r')}{k_r\cdot\alpha}+\frac{(1-r'^3)}{3}+K_M\left\{\frac{(1-r'^2)}{2}-\frac{(1-r'^3)}{3}\right\}\right] \quad (6)$$

The time taken for complete reduction θ_d will be given when r' is equated to zero. Accordingly

$$\theta_D=\frac{\alpha\rho R}{k_g(p_o-p_{H_2O}/K)}\left[\frac{k_g}{k_r\cdot\alpha}+(0.33+0.17\,K_M)\right] \quad (7)$$

Equation (7) may be compared with Equation (17) appearing in the author's paper (5):

$$\theta_D=\frac{\alpha\rho\cdot R}{k_g(p_d-p_o)}(0.33+0.17\,K_M) \quad (8)$$

It has been found on the other hand that the rate controlling step in the reduction of iron oxides with hydrogen and carbon monoxide is the counter diffusion of reactants and products (3). The equation derived [in the paper, Equation (4)] is

$$\theta=\frac{W_o\cdot r_o}{k_d\cdot A_o\cdot(p_o-p_e)}\left[\frac{3}{2}(1-r'^2)-(1-r'^3)\right] \quad (9)$$

[The dimensions of k_d is wrongly given as (g./cm./mt.) instead of (g. cm./mt. atm.).] Equation (9) has a form which is almost identical with that given in the author's paper:

$$\theta=\frac{\alpha\rho R}{k_g(p_d-p_o)}\left(\frac{K_M-1}{3}\right)\left[\left(\frac{K_M}{K_M-1}\right)\frac{3}{2}(1-r'^2)-(1-r'^3)\right] \quad (10)$$

It will be therefore seen that Equation (7) degenerates to (8) when the surface reaction is very fast (large k_r and small k_g), an assumption that has been made in the original derivation of Equation (8). On the other hand when the transport process is rapid (small R and large D_e), $(0.33 + 0.17\ K_m)$ may be neglected in comparison with $(k_g/k_r\cdot\alpha)$, (large k_g and small k_r), and Equation (7) reduces to

$$\theta_D=\frac{\rho\cdot R}{k_r(p_o-p_{H_2O}/K)} \quad (11)$$

Equation (11) is the modified form of Equation (5) appearing in the paper (*1*), evaluated for complete reduction.

It is therefore believed that in the case of noncatalytic heterogeneous reactions of the type

$$\text{A(solid)}+\text{B(gas)}\rightleftharpoons\text{C(solid)}+\text{D(gas)}$$

with a first-order kinetic equation specifying the reaction rate at the

(Continued from page 709)

INFORMATION RETRIEVAL

Key Words: Mass Transfer-8, Rinsing-8, Diffusion-8, Mechanism-8, Transport-8, Water-5, Solutions-5, Diffusivity-6, Time-6, Rinsing-7.

Abstract: The effect of contact time and diffusivity on the removal, by immersion in water of solute from a solution adhering to a flat plate was predicted from a stagnant film diffusion model and compared with experimental results. Over a three-hundredfold range of time and sixfold range of diffusivity, with dye and nitric acid solutions, the effects agreed with those of the model. The magnitude of the results gave strong indication that diffusion may be considered the controlling mechanism.

Reference: Tallmadge, J. A., B. A. Buffham, and R. R. Barbolini, **A.I.Ch.E. Journal, 8,** No. 5, p. 649 (November, 1962).

Key Words: Nitrogen Dioxide-2, Nitrogen Tetraoxide-1, Dissociation-8, Heat Transfer-8, Local Heat Transfer Coefficients-2, Colburn Analogy-8, Deissler Analogy-8, Viscosity-6, Heat Transfer and Reaction-8, Reference Enthalpy-6, Inconel-5, Computer-10.

Abstract: Local heat transfer coefficients were carefully measured for the nitrogen-nitrogen dioxide system in well-developed turbulent flow in an electrically heated, 0.194-in. I.D. tube. A modified Deissler analogy was found to predict coefficients which agreed well (0 to 19% deviation) with the observed results. The data were also compared with a simpler Colburn type of analogy in which a heat transfer coefficient based upon enthalpy was employed. The deviations here were larger.

Reference: Furgason, R. R., and J. M. Smith, **A.I.Ch.E. Journal, 8,** No. 5, p. 654 (November, 1962).

Key Words: A. Wetting-6, Packings-10, Extraction-8, Mass Transfer-7, Flooding-7, Sieve Plates-10, Surfaces-6, Column-10, Liquid-Liquid-5, Pulsed-. B. Benzoic Acid-9, Water-5, Toluene-5, Equilibrium-8, Separation-8. C. Economics-8, Energy-8, Mass Transfer-7, Column/Packed-9, Column/Sieve Plate-9, Pulsed-.

Abstract: The wetting characteristics of packings had a pronounced effect on performance of a pulsed, liquid-liquid extraction column. Unglazed ceramic packing, wet by water, gave higher flooding limits than polyethylene packing wet by the toulene phase. However mass transfer rates were higher for polyethylene packing. The use of plastic packing also resulted in a substantially lower pulsing energy requirement. Flooding limits were higher for larger size packings. Compared with a pulsed, sieve-plate column a packed column showed lower flooding limits but exhibited higher mass transfer rates. Furthermore the plastic packing required only one-fourth the energy required for a sieve-plate column for the same system at comparable conditions.

Reference: Jackson, M. L., K. L. Holman, and D. B. Grove, **A.I.Ch.E. Journal, 8,** No. 5, p. 659 (November, 1962).

(Continued on page 714)

(Continued from page 713)

INFORMATION RETRIEVAL

Key Words: Sphere-5, Carboxymethyl Cellulose-5, Drag Force-8, Drag Coefficient-8, Variational-10, Non-Newtonian-, Ostwald-De Waele-, Power Law-, Rheology-.

Abstract: A first approximation to the drag force on a sphere moving slowly through an Ostwald-de Waele fluid is obtained by means of a variational principle proposed by Pawlowski. This is the best available description of the drag force for n > 0.76; the corrected zeroth approximation of Tomita is superior for n < 0.76. Previously available experimental data are reanalyzed and compared with these developments. A zeroth approximation is given for a Sisko fluid, but no appropriate experimental data have been reported.

Reference: Slattery, John C., **A.I.Ch.E. Journal, 8,** No. 5, p. 663 (November, 1962).

(Continued on page 715)

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surface of decomposition of a spherical particle, Equation (3) represents the most general form of the expression for the instantaneous reaction rate. A more detailed investigation will appear elsewhere at an early date (*6*).

NOTATION

D = diffusion coefficient in equivalent film, sq. ft./hr.
D_e = effective diffusion coefficient in porous layers, sq. ft./hr.
k_g = mass transfer coefficient, lb./hr. sq. ft. atm. = $D/R'T \cdot Z_g$
k_r = reaction rate constant, lb./hr. sq. ft. atm.
k_d = diffusion constant, (g./cm. mt. atm.)
K = thermodynamic equilibrium constant
K_M = modified Nusselt number = $\dfrac{k_g \cdot R' \cdot T \cdot R}{D_e}$
p_{H_2O} = equivalent partial pressure of water at the interface, atm.
p_i = partial pressure of hydrogen at the interface, atm.
p_0 = partial pressure of hydrogen in the bulk gas
p_e = equilibrium partial pressure of reducing gas, atm.
$Q = k_r$ = reaction rate constant
r' = dimensionless parameter, (r/R)
r = radial position of decomposition interface, ft.
R = radius of undecomposed sphere, ft.
R' = gas constant
S = mole ratio of oxygen/iron in particle = r'^3
T = average temperature in the system, °R.
W_o = weight loss of oxide when fully reduced, g.
α = stoichiometric constant
ρ = density of original oxide, lb./cu. ft.
θ = time of decomposition, hr.

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An Analysis of Blow Over and the Steady State Bed Particle Size Distribution in a Reacting Fluid Bed

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There are fluid bed reactor situations in which the bed particles are attacked, chemically or physically, resulting in a decrease in particle size with time. Under such conditions it is necessary to feed bed material continuously to make up for losses resulting from blow over and vapor by reaction. As a consequence the steady state particle size distribution in the bed, the mass rate of blow over, and the particle size distribution in the blow over must be known. The first influences the quality of fluidization, the second determines the required capacity of the collection system, and the last will influence the type of collection system which is required.

An understanding of the behavior of fluidized beds has been the object of considerable work during the past twenty years. However much of this has been devoted to an understanding of the physical characteristics of the bed, that is gas flow patterns, particle flow patterns, and the mixing processes important within the bed. Recent work on the entrainment of particles from the bed by mechanical action of the gas usually relates entrainment to the freeboard above the bed via the exponential equation involving an entrainment constant. The work of Lewis et al. (*2*) is such a study. Fluidized bed technology has been reviewed in the text by Zenz and Othmer (*4*), in which a chapter is devoted to the process of physical entrainment.

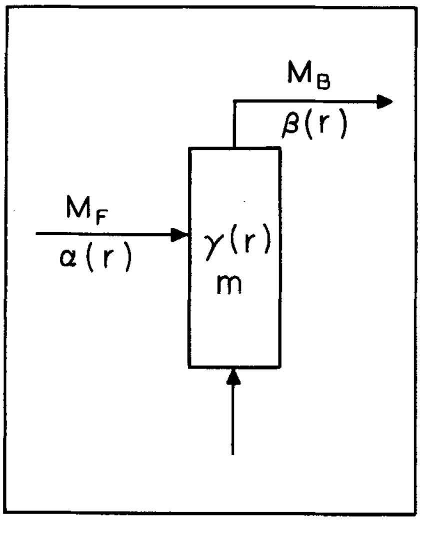

Fig. 1. Schematic of the model.

The recent contribution of Yagi and Kunii (*3*) to the understanding of particle behavior/conversion in fluidized beds is of interest. The authors present a technique for estimating the mean residence time of solids in the stream and present an elutriation velocity constant which, if it can be evaluated for situations of practical interest, permits the estimation of the average residence time of particles in the bed. However the methods for prediction of this constant for an unknown situation are not clearly so well defined as methods for its estimation for an existing and operating reactor. Furthermore a necessary assumption for the use of the techniques presented is that