

ν = kinetic viscosity [cm²/sec]
 τ = tortuosity [—]

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GAS ABSORPTION WITH CHEMICAL REACTION IN PACKED COLUMN UNDER ADIABATIC CONDITIONS*

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The absorption of carbon dioxide or sulfur dioxide into aqueous sodium hydroxide solution has been performed in a packed column, and its application to the theory of gas absorption accompanied by chemical reaction has been studied. Furthermore, the effects of the heat of solution and heat of reaction on gas absorption rate have also been investigated. The experimental values of reaction factor, which were evaluated from Eq.(7) by using the mean values of temperature and concentration at the top and the bottom of the column respectively, were in good agreement with theoretical values within an error of 30%, even though the liquid temperature difference between the inlet and the outlet of the column was as high as 30°C. Thus, the overall reaction factor in the packed column may be evaluated from Eq.(7) for other reaction systems.

A number of theoretical and experimental studies have been reported for gas absorption accompanied by chemical reaction in packed columns. Tepe and Dodge¹⁰⁾ and other investigators^{1,6)} have studied the overall capacity coefficients in packed columns for the absorption of carbon dioxide into sodium hydroxide solution when the concentration in gas phase is less than several percent. Therefore, the variation of sodium hydroxide concentration throughout the column is limited.

This paper discusses the absorption of pure carbon dioxide or pure sulfur dioxide by aqueous sodium hydroxide solutions in a packed column under adiabatic conditions. Furthermore, the effects of the heat of solution and heat of reaction on gas absorption rate are also investigated.

Experimental

The absorption column used in this study was 7.6 cm I.D. glass tube and was packed with 6 mm ceramic Raschig rings to a maximum height of 40 cm. The column consisted of a double tube evacuated and silver-coated like a vacuum bottle to avoid heat exchange through the column wall. Sodium hydroxide solution was irrigated on the top of the packed bed through a distributor with forty holes to obtain a uniform distribution. Exit liquid samples were withdrawn from the column through a sampling device fitted beneath the bottom of the packed bed to reduce the end effect. Gases of 99.8% purity were fed to the bottom of the column from commercial cylinders.

Inlet liquid temperature was adjusted to 15°C. Inlet gas temperature was also adjusted to about 15°C except for a few runs. Inlet and outlet liquid samples were analyzed for concentrations of total alkalis and

* Received on September 24, 1970

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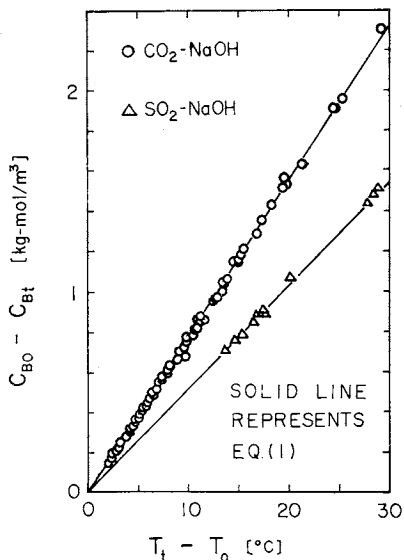
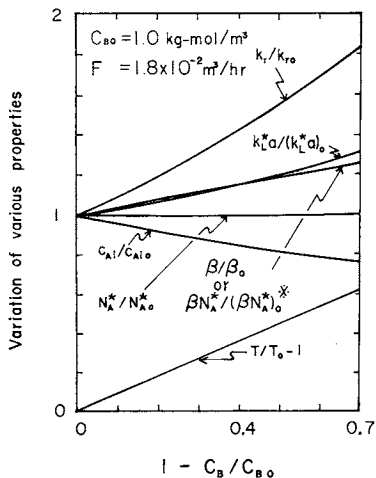


Fig. 1 Relation between the difference of concentration of NaOH and that of liquid temperature through a packed column



(*) $\beta N_A^* / (\beta N_A^*)_0$ almost coincides with β / β_0

Fig. 2 Variations of physico-chemical properties in a packed column for $\text{CO}_2\text{-NaOH}$ system

hydroxides by the Warder method, using phenolphthalein and methylorange as indicators for $\text{CO}_2\text{-NaOH}$ system and thymolphthalein and methylorange for $\text{SO}_2\text{-NaOH}$ system.

No effect of inlet gas temperature on gas absorption rate was observed, as shown in Table 1 for $\text{CO}_2\text{-NaOH}$ system. However, the liquid concentration and temperature, respectively, varied markedly throughout the column. The difference in concentration of sodium hydroxide at top and bottom of the column is plotted against that of temperature in Fig. 1. The straight lines in Fig. 1 represent the thermal equation evaluated from the following assumptions, i.e., (1) the column is at adiabatic condition, (2) the variation of temperature in the column is due to the heat of reaction and heat of solution, (3) heat generated

Table 1 Effect of inlet gas temperature on gas absorption rate for $\text{CO}_2\text{-NaOH}$ system

$z_t = 0.4 \text{ m}$, $F = 3.6 \times 10^{-2} \text{ m}^3/\text{hr}$,
feed rate of gas: $3.7 \text{ m}^3/\text{hr}$

Run	t_0 [°C]	t_t [°C]	T_0 [°C]	T_t [°C]	C_{B0} [kg-mol/m³]	C_{Bt} [kg-mol/m³]
151	25.6	16.8	15.4	40.6	2.98	1.04
154	14.2	16.1	15.5	40.2	2.98	1.06

at gas-liquid interface is transferred only to the liquid phase and (4) the heat transfer between gas and liquid phases is negligibly small. For the case when above assumptions are satisfied, liquid temperature rise is evaluated by the following equation,

$$T_t - T_0 = (C_{B0} - C_{Bt})(-\Delta H_S - \Delta H_R) / c_{P\rho} \quad (1)$$

and Fig. 1 suggests the validity of Eq.(1).

Discussion

Based on the assumption that the liquid flow is piston-like, the material balance for any differential column height, dz , leads to:

$$u \frac{dC_B}{dz} + \frac{\beta k_L^* a}{H} (C_{Ai} - C_{AL}) = 0 \quad (2)$$

where C_{AL} is considered to be zero. Thus, Eq.(2) gives:

$$u \frac{dC_B}{dz} = -\frac{\beta k_L^* a C_{Ai}}{H} = -\frac{u V \beta k_L^* a C_{Ai}}{F z_t} \quad (3)$$

with boundary conditions

$$C_B = C_{B0} \text{ at } z = 0 \quad (4)$$

$$C_B = C_{Bt} \text{ at } z = z_t \quad (5)$$

Eq.(3) is changed to dimensionless form by substituting the dimensionless quantities $Y = C_B / C_{B0}$ and $Z = z / z_t$, and then integrating with boundary conditions (4) and (5) to give:

$$\frac{FC_{B0}}{V} \int_Y^1 \frac{dY}{\beta k_L^* a C_{Ai}} = \frac{FC_{B0}}{V} \int_Y^1 \frac{dY}{\beta N_A^*} = 1 \quad (6)$$

Values of β and N_A^* in Eq.(6) change along the packed height because liquid temperature and concentration of sodium hydroxide vary in the column. Thus, Eq.(6) must be integrated graphically. At first, the concentration of sodium hydroxide was assumed appropriately for the calculation of the values of β and N_A^* . Then the liquid temperature was calculated from Fig. 1. The temperature of gas-liquid interface was estimated by the method of Kobayashi and Saito⁴⁾ or Hiraoka and Tanaka²⁾. It was nearly equal to the bulk temperature of liquid. Values of k_L^* , a and C_{Ai} were evaluated from the equations proposed by Onda et al.^{7,8)}.

Figs. 2 and 3 show the variations of $k_L^* a$, T , etc. calculated from the methods above mentioned. The variation of the product of β and N_A^* is smaller than that of other physico-chemical properties. Consequently, the product of β and N_A^* may be assumed to be constant throughout the column, and can be calculated based on the mean values of temperature and

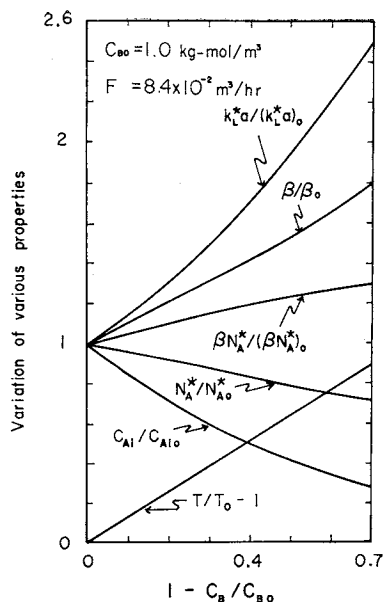
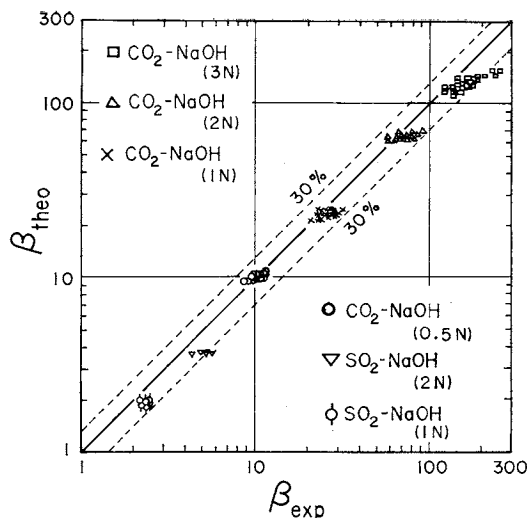


Fig. 3 Variations of physico-chemical properties in a packed column for $\text{SO}_2\text{-NaOH}$ system



Concentration in parentheses shows the initial values of sodium hydroxide.

Experimental conditions:

$z_t = 0.07 \sim 0.4 \text{ m}$, $C_{B0} = 0.5 \sim 3.0 \text{ kg-mol/m}^3$

$F = 1.8 \times 10^{-2} \sim 11.1 \times 10^{-2} \text{ m}^3/\text{hr}$

conversion of sodium hydroxide = 9~22%

Fig. 4 Comparison of the theoretical and experimental values

concentration at the inlet and the outlet of the column. Thus, Eq.(6) becomes:

$$\beta = \frac{FC_{B0}(1 - Y_t)}{VN_A^*} \quad (7)$$

In Fig. 4, the values of β obtained from Eq.(7) are plotted against the theoretical ones estimated from the film theory. In the calculation of the theoretical value of β , the reaction between carbon dioxide and sodium hydroxide is considered to be an irreversible second-order reaction as given by Nijsing *et al.*⁵⁾. The reaction between sulfur dioxide and sodium hydroxide is considered to be a two-step consecutive instantaneous chemical reaction as given by Onda *et al.*⁹⁾ or Hikita *et al.*³⁾, and reaction factor based on the film theory is evaluated by the following equations:

$$\beta = 1 + \frac{r_E}{2} \left(1 + \frac{r_{P1}}{r_{P2}} \right) q_E + r_{P1} q_P \quad (8)$$

where

$$r_E = \frac{12}{6 + Q + \kappa D_A} \frac{D_E^*}{D_A} \quad (9)$$

$$r_{P1} = \frac{-(1 + 3D_E^*/D_P^*) + \sqrt{1 + 24D_E^*/D_P^*}}{2 - D_E^*/D_P^*} \frac{D_P^*}{D_A} \quad (10)$$

$$r_{P2} = \frac{9}{3 + (Q + \kappa) D_P^*/D_B^*} \frac{D_P^*}{D_A} \quad (11)$$

$$\kappa = \sqrt{(6 - Q)^2 + 24(D_E^*/D_P^* - 1)Q} \quad (12)$$

$$Q = C_{EL}/C_{CL} \quad (13)$$

The product of β and N_A^* varied little for the systems studied in the present paper, though the liquid temperature difference between top and bottom of the column was as high as 30°C. Thus, the overall reaction factor in the packed column can be evaluated from Eq.(7) by using the mean values of temperature and concentration at top and bottom of the column respectively, and observed values of β are in good

agreement with theoretical values within an error of 30%.

Taking account of the liquid flow rate, the variation of liquid temperature in the column is considered to decrease with increasing liquid flow rate. This allows the overall reaction factor to be evaluated more accurately.

For other reaction systems, heat effect on gas absorption rate in liquid jet was negligibly small, not only for low solubility of gas, but also for high solubility of gas such as ammonia according to the result given by Onda *et al.*⁹⁾. Therefore, the overall reaction factor in a packed column for other reaction systems may be evaluated from Eq.(7) by using the mean values of temperature and concentration at top and bottom of the column, respectively.

Nomenclature

- a = interfacial area in packed bed [m²/m³]
- C_A = concentration of gaseous species in liquid phase [kg-mol/m³]
- C_B = concentration of sodium hydroxide [kg-mol/m³]
- c_P = specific heat of liquid [kcal/kg·°C]
- D_A = diffusivity of gaseous species in liquid phase [m²/hr]
- D^* = ionic self-diffusivity, subscript indicating the species [m²/hr]
- F = volumetric flow rate of sodium hydroxide solution [m³/hr]
- H = holdup [—]
- ΔH_S = heat of solution (negative for an exothermic process) [kcal/kg-mol]
- ΔH_R = heat of reaction (negative for an exothermic reaction) [kcal/kg-mol]
- k_L^* = liquid phase mass transfer coefficient [m/hr]
- N_A^* = physical absorption rate defined by $k_L^* a C_{Ai}$ [kg-mol/m²·hr]

k_r = reaction rate constant for CO₂-NaOH system [m³/kg-mol·hr]
 Q = defined by Eq.(13) [—]
 q = defined by C_L/C_{A_i} , subscript indicating the species [—]
 r_E = defined by Eq.(9) [—]
 r_{P1} = defined by Eq.(10) [—]
 r_{P2} = defined by Eq.(11) [—]
 T = liquid temperature [°C]
 t = gas temperature [°C]
 u = superficial velocity of liquid in the column [m/hr]
 V = volume of the column [m³]
 Y = dimensionless concentration of sodium hydroxide defined by C_B/C_{B0} [—]
 z = distance along the column [m]
 Z = dimensionless distance defined by z/z_t [—]
 <Greek letters>
 β = reaction factor [—]
 κ = defined by Eq.(12) [—]
 ρ = density of liquid [kg/m³]
 <Subscripts>
 C = sodium ion
 E = hydroxide ion
 F = bisulfite ion
 i = gas-liquid interface
 L = liquid bulk

P = sulfite ion
 t = top of the column
 0 = bottom of the column

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YIELD FROM REACTORS WITH RECYCLE OF REACTANTS*

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In a reactor with recycle of reactants, the relation between yield and recycle ratio of reactants is simply determined by the yield vs. feed-rate relation for single-pass operation of the reactor. If the reaction rate exhibits a maximum at a finite extent of reaction, a maximum yield is obtained at a finite recycle ratio of reactants. In this case, at yield less than the maximum value, dual values of recycle ratio are predicted for each desired yield. Operation with lower recycle ratio is only stable in a similar sense to concentration stability.

Yield from Single-pass Operation

Consider first a single reaction, for example, $A + \beta B \rightarrow \gamma R$ being carried out in a flow reactor without recycle of reactants. The yield (or the production rate) of the product R, F_R , is related to the feed rate of a specified reactant A, F_A , and to its fractional conversion at the reactor outlet, x_{Ae} , by

$$F_R = \gamma F_A x_{Ae} \quad (1)$$

Plug Flow Reactor: The yield, in this case, is obtained by

$$F_R = -V_r x_{Ae} \gamma \int_0^{x_{Ae}} \frac{dx_A}{r_A} \quad (2)$$

If the ratio of reactants, A to B, in the feed is not changed and r_A does not depend on F_A , F_R may be

expressed in terms of x_{Ae} . For a maximum value of F_R to exist at a constant value of V_r , the necessary condition causing dF_R/dx_{Ae} to vanish is

$$\int_0^{x_{Ae}} \frac{dx_A}{r_A} = \frac{x_{Ae}}{r_A(x_{Ae})} \quad (3)$$

where $r_A(x_{Ae})$ is the reaction rate at the reactor outlet condition. A maximum value of F_R at a finite value of x_{Ae} is obtained when the value of r_A changing with x_A has a maximum^{1,2)}.

This maximum in r_A is encountered in an isothermal reactor involving autocatalytic reactions, or else in a nonisothermal operation involving an exothermic reaction, especially in an adiabatic operation as pointed out by Konoki²⁾.

When $(1/r_A)$ increases monotonously with increasing x_{Ae} , dF_R/dx_{Ae} cannot vanish at $x_{Ae} > 0$. The value of F_R corresponding to $x_{Ae} = 0$ is a maximum which corresponds to $F_A \rightarrow \infty$. That this must be so

* Received on October 24, 1970