SIMULTANEOUS ABSORPTION OF CARBON DIOXIDE AND AMMONIA IN A PACKED COLUMN

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Relations for calculation of reaction factors based on the film theory have been derived for simultaneous absorption of two gases mutually reacting in the liquid phase. Algorithm is presented for calculation of mass transfer rates of both components across the interface. The calculated results were compared to experimental data on absorption rates in a packed column 110 mm in diameter packed with Rashig rings. CO_2 and NH_3 were absorbed into aqueous solutions within concentrations $0-5$ kmol/m³ CO_2 at the ratio of molar concentrations of CO_2/NH_3 equal to 0·62.

Simultaneous absorption of carbon dioxide and ammonia is widely used in industry and a great attention has been paid[1-4] to its theoretical analysis. In the refining part of the terephthalic acid process following disproportionation of potassium benzoate[5] there is necessary to absorb a gaseous mixture of CO_2 and NH_3 having a molar ratio of CO_2/NH_3 in the range $0·60-0·65$ into water solutions up to an overall saturation $5·0$ kmol/m³ CO_2 in absence of inert gases. Simultaneous absorption of theses gases has not yet been studied under these conditions. This study presents comparison of calculated absorption rates with those experimental by measured in a model packed column. Since the theoretical solution of simultaneous absorption of two mutually reacting gases[6] based on the penetration theory of mass transfer cannot be in general expressed by a functional dependence and thus its application in calculation of an absorption column is difficult, an approximate solution based on the film theory is used which results in explicit expressions for the reaction factors.

THEORETICAL

Reaction between CO_2 and NH_3 in aqueous solutions takes place in several steps where reaction $CO_2 + NH_3 \rightleftarrows NH_2COOH$ is the rate controlling step. Its kinetics is described by equation of the 2nd order with the reaction constant $k_R = 2·32 \cdot 10^6$ m³/kmol h at 30°C[7,8].

The concentration profiles of reacting components for the 2nd order reaction of the type $A + B \rightleftarrows P$ in a liquid diffusion film can be expressed according to the

film theory by solving the equations

$$D_A(d^2 c_A/dx^2) = k_R(c_A - c_A^*) c_B , \tag{1}$$

$$D_B(d^2 c_B/dx^2) = \nu k_R(c_A - c_A^*) c_B , \tag{2}$$

with boundary conditions

$$x = 0 , \quad c_A = c_A^+ , \quad c_B = c_B^+ ; \tag{3}$$

$$x = \delta , \quad c_A = c_A^0 , \quad c_B = c_B^0 . \tag{4}$$

We assume for an approximate description of the course of reaction between CO_2 and NH_3 that the reaction is fast enough to reach equilibrium already in the diffusion film and the value c_A^* is approximated by the equilibrium concentration, corresponding to the conditions in the bulk of the liquid, $c_A^* = c_A^0$.

Relations (1) to (4) can be modified by transformations

$$a = (c_A - c_A^0)/(c_A^+ - c_A^0) , \tag{5}$$

$$b = D_B c_B/[\nu D_A(c_A^* - c_A^0)] , \tag{6}$$

$$z = x/\delta_L \tag{7}$$

and by introduction of dimensionless parameters

$$M = k_R c_B^+ \delta_L^2/D_A , \tag{8}$$

$$Q = D_B c_B^0/[\nu D_A(c_A^+ - c_A^0)] , \tag{9}$$

$$R = D_B c_B^+/[\nu D_A(c_A^+ - c_A^0)] . \tag{10}$$

If we define reaction factors for the components A and B by relations

$$\Phi_A \equiv J_A^+/[k_A(c_A^+ - c_A^0)] , \tag{11}$$

$$\Phi_B \equiv J_B^+/[k_B(c_B^+ - c_B^0)] , \tag{12}$$

we get, with regard to definitions of mass transfer coefficients of both components according to the film theory and expressions for fluxes of components across the

interface, the reaction factors in the form

$$\Phi_A = -(da/dz)_{z=0} \tag{13}$$

$$\Phi_B = -(1/R)(db/dz)_{z=0} . \tag{14}$$

Double integration of the transformed differential equation (2) under transformed boundary conditions (3) and (4) results in the relation between dimensionless concentrations of reaction components

$$b = a - (R - 1 - Q)z + R - 1 . \tag{15}$$

By substitution of relation (15) into the transformed differential Eq. (1) we get the non-linear differential equation for the variable a

$$d^2a/d^2z = (M/R) a[a - (R - 1 - Q)z + R - 1] , \tag{16}$$

which cannot be solved analytically. Under the assumption of concentration b being substantially higher than concentration a in the film through which the gases are diffusing we can obtain the approximate solution of Eq. (16). The linearization of Eq. (16) is made so that values of variables for $z = 0$ are substituted into the term in square brackets. Solution of the linearized equation has, for the given boundary conditions the form

$$a = \sinh\left[(1 - z)\sqrt{M}\right]/\sinh\sqrt{M} . \tag{17}$$

The reaction factor of component A is according to relation (13) given by

$$\Phi_A = \sqrt{M}/\tanh\sqrt{M} . \tag{18}$$

Relation for the reaction factor of component B is obtained from Eqs (13) to (15) and is given by

$$\Phi_B = (\Phi_A + R - Q - 1)/(R - Q) . \tag{19}$$

Concentrations of reactions components at the interface are calculated from the relations

$$c_A^+ = p_A^+ H_A , \tag{20}$$

$$c_B^+ = p_B^+ H_B . \tag{21}$$

Partial pressures of gases at the interface are determined by solution of relations

for mass transfer in the gas phase. In our case, the convective term cannot be neglected in the relation for the net mass flux of the component to the interphase as it is usual in the case of absorption of a component present in a great excess of inert. Under the assumption that the gas mixture contains the components A and B only (at 30°C the equilibrium concentration of water vapour in gas is less than 5 mol%) holds

$$J_A = N_A + (p_A/\pi)(J_A + J_B). \tag{22}$$

The first right-hand side term in Eq (22) is the diffusion flux of the component, the second term the convective flux.

Diffusion flux of the component is given by the relation

$$N_A = -\frac{D'}{RT}\frac{dp_A}{dx} = -\frac{D'}{RT\delta_G}\frac{dp_A}{dz} = -k_G\frac{dp_A}{dz}. \tag{24}$$

By substituting N_A from Eq. (24) into Eq. (22) we get a differential equation for partial pressure of component A in the gas film and by its solution for the boundary condition

$$z = -1, \quad p_A = p_A^0 \tag{25}$$

we obtain the relation for the partial pressure of component A at the interface

$$p_A^+ = (p_A)_{z=0} = p_A^0 - \left(p_A - \frac{J_A^+}{J_A^+ + J_B^+}\pi\right)\left[1 - \exp\frac{J_A^+ + J_B^+}{k_G\pi}\right]. \tag{26}$$

A similar relation is obtained by interchange of indices which is valid for the partial pressure p_B^+.

For calculation of an absorption column the mentioned relations should be supplemented by dependences of the equilibrium concentrations of reaction components c_A^0 and c_A^0 on total analytical concentrations of CO_2 and NH_3 in solution C_A and C_B. The obtained system of equations can be then solved by iteration and the molar fluxes J_A^+ and J_B^+ can be thus determined for the given partial pressures of gases p_A^0 and p_B^0 and for the known analytical concentrations of CO_2 and NH_3. The ratio of mass fluxes of components A and B, is obtained from Eqs (9) to (12) and (19).

$$vJ_A^+/J_B = \Phi_A/(\Phi_A + R - Q - 1). \tag{27}$$

If the difference $(R - Q)$ equals to one, absorption of gases takes place in the stoichiometric ratio. If the difference is greater than one, i.e. if $D_B(c_B^+ - c_B^0) > vD_A(c_A^+ - c_A^0)$, gas B is absorbed faster, and *vice versa*.

EXPERIMENTAL

Apparatus. Column *1* (Fig. 1) of diameter 110 mm was packed with ceramic Raschig rings 15×15 mm. Height of the packing was 1 600 mm. The specific surface area of the packing was 329 m^2/m^3.

Carbon dioxide is led from a cylinder *2* through a reduction valve *3*, control valve *4* and a rotameter *5* to the top of the column *6*. Ammonia is led from a cylinder *7* through a reduction valve *8*, control valve *9* and rotameter *10* to the top of the column *11* situated below the inlet of liquid feed. After passing through the column the not absorbed gases leave at the column bottom through a water seal *12* and gas meter *13* into the atmosphere. Liquid is pumped from one of storage tanks *14* by a pump *15* through a control valve *16* and rotameter *17* to the column top. Inlet piping of the liquid feed is in the column head provided by a distributor. After passing through the column, the liquid is taken into the other tank *14* from which the feed is not pumped.

Measurements. The aim of measurements was to determine the absorption rate at constant ratio of inlet gases $NH_3/CO_2 \approx 1.6$ within the concentrations of $CO_2(NH_3)$ in absorbed solutions from 0 to 5 (0—8) $kmol/m^3$. Two series of measurements were made at constant liquid load 64·8 and 19·7 m^3/m^2 h. Gas flow rates were kept constant and were fixed so that the flow rate of the vent gas, which was controlled by a gas meter *13* accounted for approximatelly 5%
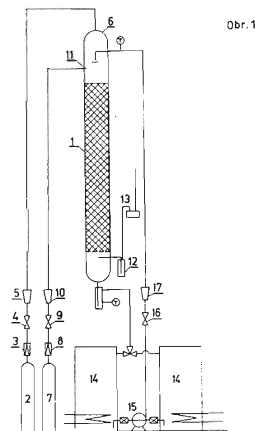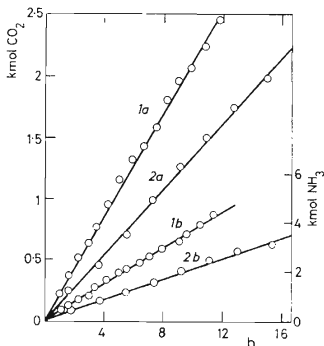

Obr.1

Fig. 1

Experimental Unit

Fig. 2

Dependence of CO_2 Absorbed on Time

1 $L = 64.8$; *2* $L = 19.7$; *a* CO_2, *b* NH_3.

of the inlet carbon dioxide. The absorption solution was collected in the product storage tank 14, volume of liquid to be fed was determined in the feed storage tank and the time of measurement was recorded.

After finishing one experiment, *i.e.* after feeding the whole content of the feed storage tank 14, samples of the liquid product were taken in which the content of NH_3 and CO_2 was determined analytically. The volume of the product solution and its temperature were recorded. The product from this absorption was used as the feed for the following experiment. In one series 10 to 20 experiments were carried out at the given liquid load and the series was finished after reaching the required concentration in the solution. In each experiment the time of the experiment was recorded and the liquid load was controlled by a material balance. The inlet feed temperature was kept at 30°C, the rise of the solution temperature after passing through the column did not exceed 5°C.

Analytical methods. Ammonia was determined by oxidimetric titration with the solution of sodium hypochlorite in the medium of sodium or potassium hydrocarbonate in the presence of bromide ions with the biamperometric indication of the equivalent point. Two polarised platinum electrodes were utilised for this purpose. Carbon dioxide was determined by the gasometric or manometric method after the decomposition of the sample by the hydrochlorid acid at higher temperature. The mean deviation of the individual analyses was found to be 3% for NH_3 and 8% for CO_2.

RESULTS

The measured data are given in Fig. 2 as a dependence of over-all absorbed quantities of CO_2 and NH_3, determined from the analytical concentrations C_A and C_B and from the measured volumes of solutions after individual experiments, on total time of experiment $\tau = \sum \Delta\tau$. The points in the graph correspond to final conditions of individual experiments.

These experimental data were compared to calculated absorption rates for the chosen parameters of the operating regime in the whole range of concentrations of CO_2 in the absorption solution. Calculations were made iteratively so that for a given quantity and composition of the initial absorption solution inlet flow rates of gases had been chosen and the column height for an 95% absorption of CO_2 was calculated. The inlet gas flow rates were corrected until the calculated height of the column corresponded to the actual height of packing. The column height was determined in step calculations starting from the top of the column with height increments 0·02 m in which the mass fluxes of gases across the interface were determined and the material balance was solved. It was again necessary to use in the calculation of mass fluxes J_A^+ and J_B^+ the iterative method which consisted of the following calculation steps: *a)* Concentrations of c_A^0 and c_B^0 were determined by solution of the equilibrium relations of Van Krevelen[9] at known over-all analytical concentrations of C_A and C_B. At the same time, the values of equilibrium constants K_1, K_2 and K_3 from the above cited paper were interpolated to the temperature of 30°C and the constant K_1 was extrapolated up to the ionic strength of the solution corresponding to $C_A = 5·0$ and $C_B = 8·0$. The obtained dependences of c_A^0 and c_B^0

on C_A for the ratio $C_A/C_B = 0.625$ are illustrated in Fig. 3. b) Partial pressure of CO_2 at the interface was assumed to be p_A^+, partial pressure of NH_3 p_B^+ was calculated from equation $\pi = p_A^+ + p_B^+$ .c. Concentrations at the interface c_A^+, c_B^+ were calculated from Eqs (20) and (21) and values of the Henry's constants taken from literature[9] were corrected to the ionic strength of the solution[10] (Fig. 3). d) Parameters M, Q, R were calculated from Eqs (8) to (10). e. Reaction factors Φ_A, Φ_B were calculated from Eqs (18) and (19). f. Mass fluxes J_A^+, J_B^+ were calculated from Eqs (11) and (12). g. The assumed partial pressure p_A^+ was checked by use of the relation (26) in which the value of the mass transfer coefficient was calculated from relation $k_G = (k_G)_{in}$ . . $(G/G_{in})^{0.7}$. In case of disagreement the partial pressure p_B^+ was calculated once more and the calculation with the new values was repeated beginning from the step c).

The calculations were made on the computer Tesla 200. Values of physical parameters were taken from literature: diffusion coefficients[11] $D_A = 7.9 \cdot 10^{-6}$, $D_B = 9.4 \cdot 10^{-6}$ (value obtained by calculation from the ratio of diffusivities from the published data[1]); reaction constant[7,8] $k_R = 2.32 \cdot 10^6$; values of the mass transfer coefficients[10] and the specific interfacial area[10] for the used liquid load $L = 64.8$: $K_A = 0.432$ extrapolated, $k_B = 0.515$ calculated from relation $k_B = k_A(D_B/D_A)$, $(k_G)_{in} = 4.93$, $a_i = 230$ extrapolated; $L = 19.7$: $k_A = 0.252$, $k_B = 0.300$ calculated from relation $k_B = k_A(D_B/D_A)$, $(k_G)_{in} = 2.54$. $a_i = 170$.
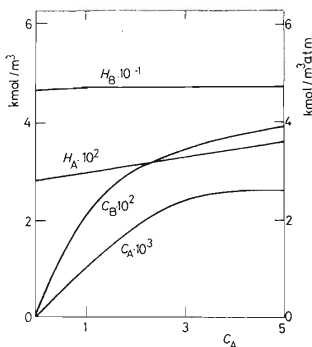

FIG. 3

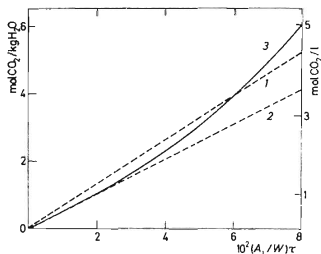Calculated Dependences of H and $C°$ on C_A

FIG. 4

Comparison of Experimental and Calculated Absorption Rates

1 $L = 64.8$; 2 $L = 19.7$; 3 theoretical.

Calculation simulating the absorption in a given set of experiments resulted in the time dependence of C_A. From these calculations resulted that the mean mass fluxes of components across the over-all interfacial area do not practically depened on the liquid flow rate within the studied range and are strongly dependent only on the inlet concentration of the absorption solution. It was therefore possible to represent the calculated results in the form of a single dependence of concentration CO_2 (mol CO_2/kg H_2O on parameter $\tau A_i/W$ together for both series of experiments. Since the water amount W and the liquid load affecting the interfacial area A_i did not vary in the whole series of experiments, the slope of this functional dependence gives the mean value of mass flux in the whole column. This calculated dependence is presented as the curve *3* together with the curves *1* and *2* representing the experimental results (see experimental data in Fig. 2) in Fig. 4. Mass fluxes of components are, of course, variable along the height of the column. Calculations have shown that the absorption rate of ammonia is at the inlet of gases into the column approximatelly ten-times faster than absorption of carbon dioxide. Absorption of ammonia prevails in the upper tenth of the column height where more than 95% of the inlet ammonia is absorbed. Absorption under conditions at the inlet of gases is illustrated by calculated concentration profiles of absorbed components in diffusion films, which are plotted in Fig. 5a. In the lower part of the column there prevails absorption of carbon dioxide while in the region of outlet of the gases from the column there is practically no ammonia present. The calculated concentration profiles in diffusion films for conditions at the outlet from the column are illustrated in Fig. 5b.
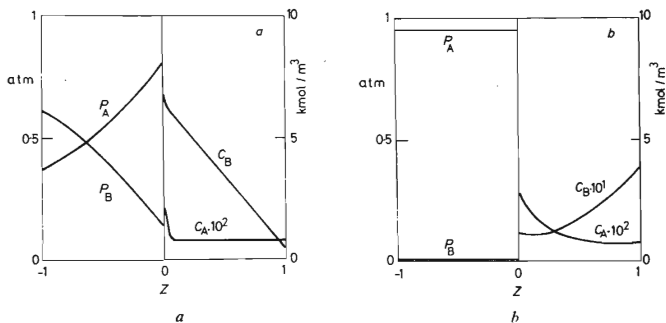

FIG. 5

Concentration Profiles in Diffusion Films

a At the column inlet, *b* at the column outlet.

DISCUSSION

Comparison of experimental results with those calculated ones as illustrated in Fig. 4 demonstrates that in the region of lower saturation of the absorption solution up to about 2·5 kmol/m³ of CO_2 (4 kmol/m³ NH_3) there is quite a good agreement of the experimental results with those calculated. In the region of higher concentrations, the calculated values of the absorption rates tend to deviate to higher values. This discrepancy may be explained by the inaccuracy of the equilibrium data used in the calculation as these data have been considerably extrapolated from the region of lower concentrations. Also some accumulation of inert gases in the absorption column can result in a decrease of partial pressures of absorbed gases and can thus slow down the rate of absorption. In this plot the slopes of curves representing the experimental results of two series differ by about 20%. This deviation can be most probably ascribed to an inaccurate estimation of the interfacial area that was determined on basis of an empirical correlation (Onda[10]) extrapolated for higher feed rates which had not been verified for the co-current arrangement of phase flows. These deviations cannot be explained by an error in the determination of mass transfer coefficients, since as the calculation has shown, these values cannot have under the experimental conditions any significant effect on mass fluxes. Under these conditions absorption of carbon dioxide approaches the so-called regime of fast reaction in which the mass flux of component A is determined by the value of expression $J_A^+ = (k_R D_A c_B^+)^{1/2}$. Under appropriately chosen experimental conditions it would be possible to use this system for determination of the effective interfacial area of an absorption unit. Under conditions at the inlet of gases into the column (Fig. 5a), when there is a relatively high partial pressure of ammonia, the reaction takes place in close vicinity of the interphase boundary. High mass flux of ammonia with respect to the flux of carbon dioxide causes an increase in partial pressure of CO_2 in direction to the interphase boundary which favourably affects the rate of absorption of CO_2. Under conditions at the outlet of gases from the column with partial pressure of ammonia being very low, practically only absorption of CO_2 takes place and the reaction zone extends from the interface approximatelly up to one half of the liquid diffusion film thickness and ammonia necessary for the reaction is provided mostly from the bulk of liquid (Fig. 5b). The results on simultaneous absorption of CO_2 and NH_3 clearly demonstrate that for attaining a maximum saturation of the absorption solution by carbon dioxide, the co-current arrangement of absorption is more advantageous than the countercurrent one. The cocurrent arrangement is especially preferable for absorption with zero or low liquid recirculations.

LIST OF SYMBOLS

a	reduced concentration of component A
a_i	effective interfacial area (m^2/m^3)
A_i	interfacial area (m^2)
b	reduced concentration of component B
c	concentration of reaction component $(kmol/m^3)$
c_A^*	equilibrium concentration of component A $(kmol/m^3)$
C	over-all analytical concentration $(kmol/m^3)$
D	liquid-phase diffusivity (m^2/h)
D'	gas-phase diffusivity (m^2/h)
G	gas flow rate $(kg/m^2\ h)$
H	Henry's law constant $(kmol/m^3\ atm)$
J	mass flux $(kmol/m^3\ h)$
J^+	mass flux across the interface $(kmol/m^3\ h)$
k	mass transfer coefficient (m/h)
k_R	reaction rate constant $(m^3/kmol\ h)$
K	equilibrium constant of reaction $(m^3/kmol)$
L	liquid feed rate $(m^3/m^2\ h)$
M	parameter defined by Eq. (8)
N	diffusion flux $(kmol/m^2\ h)$
p	partial pressure (atm)
Q	parameter defined by Eq. (9)
R	parameter defined by Eq. (10)
$\boldsymbol{R}$	gas constant $(m^3\ atm/kmol\ deg)$
T	temperature (K)
W	amount of water in the absorption solution (kg)
x	distance from the interface (m)
z	dimensionless distance from the interface
δ	thickness of the film (m)
ν	stoichiometric coefficient
π	total pressure (atm)
τ	time (h)
Φ	reaction factor

Subscripts

A	component A (CO_2)
B	component B (NH_3)
P	reaction product
G	in gas phase
L	in liquid phase
in	at the column inlet

Superscripts

$+$	at the interface
0	in the bulk of liquid
$*$	at chemical equilibrium

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