Absorption with an Infinitely Rapid Chemical Reaction in Packed Towers

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A mathematical treatment of gas absorption accompanied by an infinitely rapid, liquid phase reaction has been carried out by Hatta (*1*) for the case of the two-film hydrodynamic model. This analysis has been useful for the interpretation of absorption data obtained in equipment which has permitted direct application of the rate equations to the experimental results. However the equations have been of little use for analyzing the operation of a packed tower because the theory does not relate the changes in stream compositions to the length of the apparatus but rather confines consideration to absorption taking place from a gas of constant composition. Since algebraic expressions for the tower height in cases of absorption with chemical reaction have been conspicuously absent from the literature, it seems opportune to demonstrate that in the case of an infinitely rapid reaction such an expression can be readily obtained.

A solute gas A is absorbed from a gas mixture by a solution containing the dissolved substance B, with which A is assumed to react instantaneously, in accordance with the equation

$$A + rB \rightarrow AB_r$$

Derivations of the Hatta theory equations are given by Hatta (*1*) and Sherwood and Pigford (*2*) with the following results:

$$N_A = k_G p \qquad \text{for } q \geqq q_c \qquad (1)$$

$$N_A = \frac{\dfrac{p}{H} + \dfrac{D_B \rho\, q}{D_A r}}{\dfrac{1}{k^\circ_L} + \dfrac{1}{H k_G}} \qquad \text{for } q \leqq q_c \quad (2)$$

where $q_c = \dfrac{D_A k_G p r}{D_B k^\circ_L \rho}$

q_c has been termed the "critical concentration." If absorption takes place at constant temperature and constant total pressure from a gas of constant composition into a solution in which the bulk concentration of B is above the critical value, the theory predicts that the rate of absorption remains constant as q decreases to the critical value. The rate then falls off linearly with q as indicated by Equation (2), on the assumption that the other quantities in Equation (2) remain constant. When component B is completely reacted, absorption occurs by physical solution of A.

In general for packed tower operation of the type being considered, there are three zones in the tower, absorption following a different rate equation in each. These zones are shown in Figure 1. It is assumed that in any plane perpendicular to the tower axis all conditions are constant. At the top of the tower there is a zone in which the absorption rate is completely determined by the gas phase resistance and is given by Equation (1). In this zone the reaction occurs at the liquid surface. As the liquid flows down through the tower, q decreases and p increases. At some point the value of q_c is reached. Absorption then follows Equation (2) until all the dissolved reactant B is used up. In this middle zone the reaction occurs in a plane parallel to the interface in the interior of the liquid. Below the level in the tower at which reactant B is used up mass transfer occurs by physical solution of A into a solution of AB_r in accordance with the usual expression

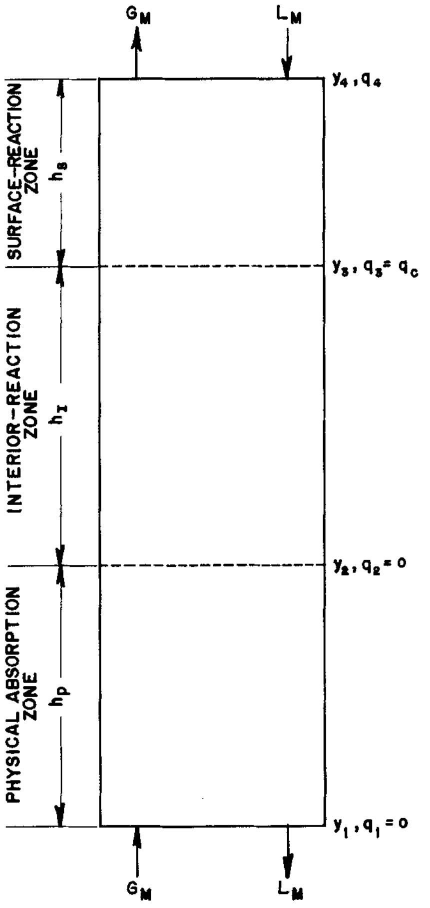

Fig. 1. Representation of the three absorption zones in a packed tower in which the reaction $A + rB \rightarrow AB_r$ takes place at an infinitely rapid rate.

$$N_A = K_G(p - p_e) \qquad (3)$$

Depending on the conditions of operation and the gas-liquid system, one, two, or all three zones may exist in an absorption tower. Since a different absorption equation governs the mass transfer process in each zone, a separate design equation must be developed for each of the three sections of the tower.

For the surface-reaction zone a material balance for a differential length of tower is given by

$$N_A a = G_M \frac{dy}{dh} \qquad (4)$$

and the rate equation is

$$N_A a = k_G a y P \qquad (5)$$

Assuming $(G_M/k_G aP)$ to be constant one gets

$$h_S = \frac{G_M}{k_G aP} \ln \frac{y_3}{y_4} \qquad (6)$$

For the interior-reaction zone the differential material balance is Equation (4), and the rate equation is Equation (2). Combining these one obtains

$$G_M \frac{dy}{dh} = \frac{p + \dfrac{D_B H \rho q}{D_A r}}{\dfrac{1}{k_G a} + \dfrac{H}{k^\circ_L a}}$$

$$= K_G aP \left[y + \frac{D_B H \rho\, q}{D_A r P} \right] \qquad (7)$$

It is convenient to redefine the Henry's law constant in terms of mole fractions as $m = \rho H/P$, which gives

$$G_M \frac{dy}{dh} = K_G aP \left[y + \frac{D_B m q}{D_A r} \right]$$

A material balance over a portion of the tower gives

$$q = q_c - \frac{G_M r}{L_M} (y - y_3) \qquad (9)$$

Substituting Equation (9) into Equation (8) one gets

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$$\frac{dy}{dh}=\frac{K_GaP}{G_M}\left[\left(1-\frac{mG_MD_B}{L_MD_A}\right)y+\frac{mq_cD_B}{rD_A}+\frac{mG_MD_{By3}}{L_MD_A}\right] \qquad (10)$$

Equation (10) is of the form

$$\frac{dy}{dh}=\frac{K_GaP}{G_M}(\alpha y+\beta) \qquad (11)$$

where α and β are constants*. Separating the variables and integrating, assuming (G_M/k_GaP) constant, one obtains

$$h_I=\frac{\dfrac{G_M}{K_GaP}\ln\left[\left(1-\dfrac{mG_MD_B}{L_MD_A}\right)\left[\dfrac{y_2+\dfrac{mq_cD_B}{rD_A}}{y_3+\dfrac{mq_cD_B}{rD_A}}\right]+\dfrac{mG_MD_B}{L_MD_A}\right]}{\left(1-\dfrac{mG_MD_B}{L_MD_A}\right)} \qquad (12)$$

The equation for the tower height in the physical absorption zone is the same as the one derived by Colburn (3) for physical absorption, namely

$$h_p=\frac{\dfrac{G_M}{K_GaP}\ln\left[\left(1-\dfrac{mG_M}{L_M}\right)\left(\dfrac{y_1}{y_2}\right)+\dfrac{mG_M}{L_M}\right]}{\left(1-\dfrac{mG_M}{L_M}\right)} \qquad (13)$$

The total tower height is

$$h=h_S+h_I+h_p \qquad (14)$$

In order to use Equation (12) the value of q_c must be found. When one refers to Figure 1, the following material balance may be written:

$$y_3=\frac{L_M}{G_Mr}(q_4-q_c)+y_4 \qquad (15)$$

By definition

$$q_c=\frac{D_Ak_Gy_3Pr}{D_Bk^\circ_L\rho} \qquad (16)$$

When one combines Equations (15) and (16)

$$q_c=\frac{\dfrac{D_Ak_GPL_M}{D_Bk^\circ_L\rho G_M}q_4+\dfrac{D_Ak_GPr}{D_Bk^\circ_L\rho}y_4}{1+\dfrac{D_Ak_GPL_M}{D_Bk^\circ_L\rho G_M}} \qquad (17)$$

The application of Equations (12) and (13) requires that y_2 be known; it is easily calculated by means of the material balance

$$y_2=y_4+\frac{L_Mq_4}{G_Mr} \qquad (18)$$

The terminal conditions, y_1, y_4 and q_4 are of course known.

Equation (12) for the height of tower in the interior-reaction zone shows a marked similarity in form to Equation (13) derived by Colburn (3) for physical absorption. Colburn gives a convenient graphical solution of Equation (13) in Figure 1 of his paper. This figure may also be used for Equation (12) if the abscissa is changed to

$$\frac{y_2+\dfrac{mq_cD_B}{rD_A}}{y_3+\dfrac{mq_cD_B}{rD_A}}$$

and the parameter to

$$\frac{mG_MD_B}{L_MD_A}$$

For absorption followed by a rapid reaction in a packed tower it is in general not possible to describe the operation of the column with a single rate equation. The existence of zones consisting of longitudinal segments of the column each of which has its own separate rate equation is fundamental to the analysis of the problem.

There is ample evidence that when absorption is followed by an irreversible chemical reaction the effective mass transfer area is greater than in the case of absorption without reaction (4). Therefore, if physical absorption data are used to obtain k_Ga and K_Ga for use in Equations (6) and (12), it will be necessary to correct the mass transfer coefficients by means of a method such as that of Shulman, Ullrich, and Wells (4) which enables one to calculate k_Ga for the surface-reaction zone when the physical-absorption value of k_Ga is known. The influence of the reaction on the effective interfacial area in the interior-reaction zone has apparently never been studied. It is likely that the effective area in the interior-reaction zone is intermediate between the area for physical absorption and the area for the surface-reaction zone. However a precise numerical evaluation of the increase in effective area brought about by the reaction in the interior-reaction zone is not possible at present.

It will be noted from Equation (17) that the critical concentration q_c is independent of the interfacial area. The film coefficients appear as the ratio $(k_G/k^\circ_L)=(k_Ga/k^\circ_La)$ and are obtained from physical absorption data.

NOTATION

a = area of interphase contact, sq. ft./cu. ft.
D_A = diffusion coefficient of A in the liquid, sq. ft./hr.
D_B = diffusion coefficient of B in the liquid, sq. ft./hr.
G_M = superficial molal gas rate, lb.-moles/(hr.)(sq. ft.)
h = total column height, ft.
h_I = column height in the interior-reaction zone, ft.
h_P = column height in the physical absorption zone, ft.
h_S = column height in the surface-reaction zone, ft.
H = Henry's law constant, (atm.)(cu. ft.)/lb.-mole
k_G = gas-film coefficient, lb.-moles/(hr.) (sq. ft.) (atm.)
k°_L = liquid-film coefficient in the absence of chemical reaction, lb.-moles/(hr.)(sq. ft.) (lb.-mole/cu. ft.)
k_Ga = gas-film coefficient, lb.-moles/(hr.)(cu. ft.)(atm.)
k°_La = liquid-film coefficient in the absence of chemical reaction, lb.-moles/(hr.) (cu. ft.) (lb.-moles/cu. ft.)
K_Ga = over-all mass transfer coefficient (in the absence of chemical reaction), lb.-moles/(hr.)(cu. ft.)(atm.)
L_M = superficial molal liquid rate, lb.-moles/(hr.)(sq. ft.)
m = Henry's law constant based on mole fractions
p = partial pressure of A in the bulk gas stream, atm.
p_e = partial pressure of A in equilibrium with the liquid phase, atm.
P = total pressure, atm.
q = mole fraction of B in the bulk of the liquid
q_c = $(D_Ak_Gpr/D_Bk^\circ_L\rho)$
q_1 = mole fraction of B in the liquid leaving the physical absorption zone of the column
q_2 = mole fraction of B in the liquid entering the physical absorption zone of the column
q_3 = mole fraction of B in the liquid entering the interior-reaction zone of the column
q_4 = mole fraction of B in the liquid entering the surface-reaction zone of the column.
r = molecules of B reacting with one molecule of A

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* When α and β cannot be assumed constant, a graphical solution can be used.

y = mole fraction of A in the bulk gas stream

y_1 = mole fraction of A in the gas entering the physical absorption zone of the column

y_2 = mole fraction of A in the gas entering the interior-reaction zone of the column

y_3 = mole fraction of A in the gas entering the surface-reaction zone of the column

y_4 = mole fraction of A in the gas leaving the surface-reaction zone of the column

$\alpha = 1 - \dfrac{mG_MD_B}{L_MD_A}$

$\beta = \dfrac{mq_cD_B}{rD_A} + \dfrac{mG_MD_By_3}{L_MD_A}$

ρ = molal density of the liquid, lb.-moles/cu. ft.

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Solubility of Cyclohexane in Water

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An experimental study was made on the solubility of cyclohexane in water at pressures to about 425 lb./sq. in. abs. and at temperatures of 100°, 160°, 220° and 280°F. No solubility data for cyclohexane in water have been found in the literature. However the solubility of water in cyclohexane is reported by Tarassenkow and Poloshinzewa (*4*) at temperatures from 14° to 52°C. and at total pressure of the system.

The experimental technique and the analytical procedure have been described in detail previously (*2*). No changes were made in the equipment for the present investigation.

MATERIALS

The cyclohexane used in the present study was pure grade stock and is certified to have a minimum purity of 99.0 mole%. A gas chromatography analysis of the hydrocarbon showed the purity to be about 99.6% cyclohexane. The water was taken from the distilled water source of the laboratory and was boiled to remove any dissolved gases.

EXPERIMENTAL RESULTS

The smoothed data are shown in Table 1.

For comparative purposes the solubilities of cyclohexane and that of cyclopropane in water (*3*) are plotted in Figure 1. These curves show a decrease in solubility with the increase in molecular weight (*1*). The minimum solubility phenomenon is not present in either the cyclopropane-water system or the cyclohexane-water system in the pressure and temperature range of investigation.

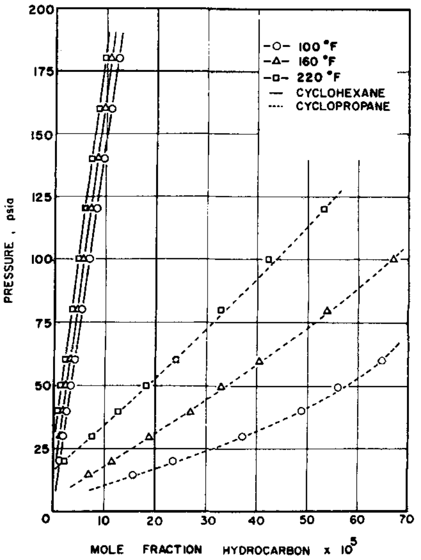

Fig. 1. Comparative solubility of cycloparaffins in water.

TABLE 1. SMOOTHED DATA—SOLUBILITY OF CYCLOHEXANE IN WATER

(Mole Fraction Cyclohexane × 10^5)

Total pressure, lb./sq. in. abs.	100°F. (3.25*)	160°F. (10.93*)	220°F. (28.96*)	280°F. (62.33*)
14.7	0.97	0.58	—	—
20.0	1.34	1.00	—	—
30.0	2.03	1.60	0.72	—
40.0	2.72	2.20	1.32	—
50.0	3.41	2.83	1.92	—
60.0	4.10	3.45	2.51	0.70
80.0	5.48	4.71	3.70	1.91
100.0	6.85	5.92	4.89	3.13
120.0	8.22	7.18	6.05	4.40
140.0	9.6	8.43	7.27	5.62
160.0	11.03	9.71	8.48	6.82
180.0	12.4	10.92	9.69	7.95
200.0	13.8	12.28	10.8	9.08
250.0	17.08	15.41	13.92	12.1
300.0	20.2	18.24	16.68	14.6
350.0	23.11	21.0	19.2	—
400.0	25.84	23.61	21.52	—
450.0	28.35	25.98	23.46	—

* Vapor pressure of pure cyclohexane.

ACKNOWLEDGMENT

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