CHAPTER 4

GENERAL CONSIDERATIONS

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The relevant equations which can be utilised for estimating the values of true gas side and liquid side mass transfer coefficients (k_G and k_L), also the liquid side coefficient with chemical reaction (k_L') have been outlined in this chapter. Estimation of different parameters like Henry's law constant for gas absorption in water (H), Henry's law constant for absorption in electrolyte solutions (H'), diffusivity (D), reaction velocity constant (k) and surface tension (σ) etc, for different systems pertaining to gas absorption without chemical reaction and gas absorption accompanied by chemical reaction has also been critically surveyed.

4.1.0 ESTIMATION OF k_G FROM $K_G a$ DATA (FOR ABSORPTION WITHOUT CHEMICAL REACTION)

The interrelation between the overall gas side mass transfer coefficient for physical absorption ($K_G a$), the true gas and liquid side mass transfer coefficients (k_G and k_L respectively), the interfacial area available for mass transfer ($\dot{a}$) and Henry's law constant (H) is expressed by equation (4.1).

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{H}{k_L a} \tag{4.1}$$

Thus, in order to obtain the values of k_G from K_Ga values, one requires the knowledge of k_La, 'a' and H. The values of k_La and 'a', required for estimation of k_G by using equation (4.1), could be evaluated under identical conditions by using the under mentioned generalised correlations [Equations (4.2) and (4.3)]:-

$$k_La = C\ (Re)^{\alpha}\ (We)^{\beta}\ (Fr)^{\gamma}\ (\sigma / \sigma_c)^{\delta}\ Sc^{m}\ (\rho_L / \mu_L g)^{n}\ a_t \qquad (4.2)$$

$$a / a_t = C\ (Re)^{\alpha}\ (We)^{\beta}\ (Fr)^{\gamma}\ (\sigma / \sigma_c)^{\delta} \qquad (4.3)$$

where, Re is the Reynold's number $(L/a_t \mu_L)$, We is the Weber number $(L^2/ \rho_L a_t \sigma)$, Fr is the Froude number $(a_t L^2/ \rho_L{}^2 g)$, Sc is the Schmidt number $(\mu_L/ \rho_L D_L)$ and (σ / σ_c) is a parameter defining wetting characteristics of the packing material.

Estimation of H for the case of physical absorption has been discussed separately. Thus, by knowing the values of k_L, 'a' and H, the values of k_G can be computed from K_Ga data.

4.1.1 Estimation of k_G from H_{OG} data for vaporization of pure solvents

To obtain the values of the true gas side mass transfer coefficient (k_G) from the values of height of overall gas side transfer unit (H_{OG}), it is necessary to evaluate initially the values of overall gas side mass transfer coefficient (K_Ga) using equation (4.4).

$$K_Ga = \frac{G_m}{H_{OG}\ P} \qquad (4.4)$$

where G_m is the molar velocity of the gas phase and P is the pressure.

Further, in case of pure solvents, due to non existence of the liquid side resistance to mass transfer, the values of K_Ga and k_Ga become identical. Therefore, by estimating the value of the effective interfacial area during vaporization using a generalised correlation of type equation (4.3), the value of k_G could be conveniently obtained from H_{OG} data.

4.2.0 ESTIMATION OF $k_L'a$ FROM K_Ga DATA FOR ABSORPTION WITH CHEMICAL REACTION

The interrelation between the overall gas side mass transfer coefficient for chemical absorption (K_Ga), the true gas side coefficient (k_G), the liquid side coefficient with reaction (k_L'), the effective interfacial area during chemical absorption (a_c) and the Henry's law costant for electrolyte solutions (H') is expressed by equation (4.5).

$$\frac{1}{K_Ga} = \frac{1}{k_Ga} + \frac{H'}{k_L'a} \qquad (4.5)$$

Therefore, to obtain the values of the volumetric liquid side coefficient with reaction ($k_L'a$), the knowledge of k_G, 'a' and H' are essential. The values of 'a' could be obtained by a generalised correlation - equation (4.3) and k_G can be estimated by the under mentioned generalised correlation equation (4.6):-

$$k_G = C \ (Re_G)^{\alpha} \ (Sc_G)^{m} \ (a_t d_P)^{n} \ (RT/a_t \ D_G)^{\varepsilon} \qquad (4.6)$$

where Re_G and Sc_G are the Reynolds number and Schmidt number for the gas phase.

Estimation of H' has been discussed separately. Thus by knowing the values of k_G, 'a' and H', the value of $k_L'a$ can be computed from K_Ga data.

4.3.0 ESTIMATION OF DIFFERENT PARAMETERS :

4.3.1 Estimation of Henry's law constant :

(I) Estimation of Henry's law constant (H) for absorption of gases into water :

The values of H requried in the present investigation for the systems - (i) CO_2-water, (ii) acetone-water, (iii) methanol-water, (iv) ethanol-water and (v) ammonia-water can be calculated by using the following equations :-

$$\log S_w = (A/T) - B \tag{4.7}$$

$$H = (1/S_w) \tag{4.8}$$

where S_W is the solubility of these gases in water
A and B are empirical constants and T is the temperature (K).

For system - (i), the values of solubility are directly obtained in MKS units (3), however for the systems (ii), (iii) and (iv) the values of constants being in FPS units(47,48), the value of S_W obtained by equation (4.7) should be multiplied by a factor 16.018 to obtain values in MKS units (k mol/m^3 atm).

In the case of system - (v) : Ammonia - Water, one should use equation (4.9) instead of equation (4.7).

$$\ln \frac{M}{P} = \frac{A}{T} - B \qquad (4.9)$$

where M is the Molality (gm mol/kg of solution)
and P is the pressure (atm).

The values of S_W are calculated by multiplying the resulting M/P values [expressed as (k mol/kg solution)/atm] with density of the solution (ρ_L). The constants to be utilised in equation (4.7) and equation (4.9) are listed below :

System	(i)	(ii)	(iii)	(iv)	(v)
Constant A	1140	2125	2325	2250	4425
Constant B	5.3	6.95	6.678	6.469	10.82

(II) Estimation of Henry's law Constant (H') for absorption of gas in electrolyte solutions :

In electrolyte solutions, H' can be estimated by the method of Van Krevelen and Hoftijzer (145), wherein Henry's law constant in the solution to that in water (ratio of H' to H) at the same temperature is interrelated as under:-

$$\log \left(\frac{H'}{H}\right) = h_1 I_1 + h_2 I_2 + \ldots\ldots \qquad (4.10)$$

where H'/H is the ratio of Henry's Law constant in the solution to that in water. Further $h = h_+ + h_- + h_G$, the sum of contributions due to cation, anion and the species of gas respectively and h_1, h_2 are values of h for individual electrolytes having ionic strengths

I_1, I_2 etc. Barret (146,147) and Onda (148) have given the values of h for various ions and gas species. In this work, the values of h given by Barret have been utilised for all other systems except for the systems : CO_2-monoethanolamine and CO_2-diethanolamine solutions. For these systems, the values of h given by Onda have been considered with the contribution of ethanolamine taken as that of ammonium bicarbonate as mentioned by Danckwerts and Sharma (3).

For CO_2 absorption in partially carbonated monoethanolamine, equation (4.11) suggested by Hikita et al. (149) could be used for estimating the value of H'.

$$\log \left(\frac{H'}{H} \right) = hI - \frac{0.3\,(MEA)}{1 + k\,(MEA)} \qquad (4.11)$$

where k is an empirical constant reported in the above reference.

4.3.2 Estimation of physical properties :

The relevant information available in the references (150-174) could be utilised conveniently to obtain the values of physical properties like density, viscosity, surface tension, diffusivity and reaction velocity constant pertaining to different solute gases, solvents and corresponding systems.

(i) Density and Viscosity

System/Component	Density	Viscosity.
Water	(150)	(150,160)
Methanol, Methanol-Water	(150,151)	(150,151)
Isopropanol - Water	(150,152)	(152,160)
Isobutene-Sulfuric acid-Water	(26,153)	(26,153)
Hydrocarbon solvents	(154,155)	(150,161)
Electrolyte Solutions.	(155,156)	(155,156)
Ethanolamines.	(158,159)	(158,159)
Gases and Vapours.	-	(160)
Freon 12.	(162)	(150,162)

(ii) Surface Tension :

Surface tension values of water, organic solvents, aqueous solutions and electrolyte solutions, etc could be obtained from references (156,157,163,164). Surface tension values of ethanolamine solutions at various temperature can be calculated by the method of Tamara, Kurata and Odani (165,166). When pure gases are used, the surface tension values should also be corrected for pure gas interface as mentioned in the International Critical Table (163).

(iii) Critical Surface Tension :

The values of critical surface tensions for ceramic, steel glass, polyethylene, PVC have been reported by Onda (97). For the other packing materials namely hydrophilised polymeric packings, polypropylene and PTFE packings, the values of critical surface tension mentioned in literature references (35,167 to 169) are 54, 27.7 and 18 mN/m respectively.

(iv) Diffusivity :

The value of diffusivity (D_L) for CO_2 in water has been reported as 1.97 x 10^{-9} m^2/s at 25°C by Scriven and Pigford (170,171). The values of diffusivity of O_2 and H_2 in water have been reported by Vivian and King (172). Diffusivity of CO_2 in ethanolamine solutions could be evaluated by the calculational method proposed by Danckwerts and Sharma (3).

The Stoke's Einstien equation can be utilised conveniently for estimating the values of diffusivities at various temperatures for electrolye as well as non-electrolyte solutions.

$$(D_L \mu_L / T) = \text{constant} \qquad (4.12)$$

Diffusivities could also be estimated in electrolyte solutions, using the following relationship proposed by Ratcliff and Holdcroft (173):-

$$D_L \mu_L^{0.637} = \text{constant} \qquad (4.13)$$

Diffusivity of vapours and gases in air can be estimated by under mentioned equation (4.14) given in International Critical Tables (174).

$$D_G = D_o (T/T_o)^m (P_o/P) \qquad (4.14)$$

where D_o is the diffusivity of the vapour/gas at P_o (1 atm) and T_o (273° K), the value of m for different gases are given in reference (174).

However for estimating the diffusivity of water vapour in Freon-12, one has to use undermentioned equation (4.15), which is the Wilke and Lee (175) modification of the equation by Hirschfelder Bird and Spotz (176).

$$D_{12} = [10.7 - 2.46 (M)^{0.5}] T^{1.5} (M)^{0.5} / (P r_{12}^2 w_{(1)}^1) \quad (4.15)$$

where $M = [(M_1 + M_2)/M_1 M_2]^{0.5}$, M_1 and M_2 are molecular weights, T is temperature in (K), P is the total pressure, r_{12} is the collison diameter and $w_{(1)}^1$ is the collision integral for diffusion the values of r_{12} and $w_{(1)}^1$ could be estimated from the figures and tables given by the investigators.

(v) Estimation of reaction velocity constants :

k_{OH} for system CO_2-NaOH :

The second order rate constant for the reaction between CO_2 and the hydroxyl ion (k_{OH}) could be obtained by the under mentioned modified Pinsent equation proposed by Astarita (177).

$$\log k_{OH} = 13.635 - \frac{2895}{T} + 0.08\ I \quad (4.16)$$

where T is the temperature (K) and I is the ionic strength of the solution.

k_{NH_3} for system CO_2-NH_3 :

The values of the second order reaction rate constant (k_{NH_3}) for the reaction between CO_2 and NH_3 could be calculated by equation (4.17) which was proposed by Pinsent, Pearson and Roughton (178).

$$\log k_{NH_3} = 11.13 - \frac{2530}{T} \quad (4.17)$$

where T is the temperature (K)

k_{MEA} for system CO_2-MEA :

The values of the second order reaction velocity constants reported by Sharma (3) at temperatures of 18°, 25° and 35° C could be extrapolated to obtain the values of k_{MEA} in the temperature range 40° to 50° C.

k_3 for system CO_2-DEA :

The reaction between CO_2 and DEA follows third order kinetics (first order with respect to CO_2 and second order with respect to DEA) as reported by Hikita et al (179). Hence, the value of k_3 - third order reaction velocity constant - can be estimated by using equation (4.19).

$$\log k_3 = 12.41 - \frac{2775}{T} \qquad (4.18)$$

where T is temperature (K).

4.4.0 ESTIMATION OF HETP FROM k_La, k_V and a_d :

The interrelation between the height equivalent of a theoretical plate (HETP) and the height of overall transfer unit in terms of vapour composition (H_{OV}) is expressed as under:-

$$HETP = \frac{\ln \lambda}{\lambda - 1} H_{OV} \qquad (4.19)$$

where λ is the ratio of slope of equilibrium line to the operating line.

H_{OV} is related to the height of liquid phase transfer unit (H_L) and the height of vapour phase transfer unit (H_V) by under mentioned equation (4.20).

$$H_{OV} = H_V + \lambda H_L \qquad (4.20)$$

Further, H_L and H_v values can be computed from knowledge of the values of the liquid side and vapour side mass transfer coefficients k_L and k_V respectively, by the following equations:-

$$H_L = \frac{L}{k_L a \rho_L} \qquad (4.21)$$

$$H_v = \frac{G}{k_V a_d P M_{avg}} \qquad (4.22)$$

where L and G are the liquid and vapour rates, ρ_L is the liquid density, P is the total pressure, M_{avg} is the average molecular weight of the vapour phase and 'a_d' is the area of mass transfer.

The values of $k_L a$, k_V and 'a_d' required for estimating H_L and H_V can be obtained using generalised correlations of type given by equations - (4.23) to (4.25).

$$k_L a = C\,(Re)^{\alpha}\,(We)^{\beta}\,(Fr)^{\gamma}\,(\sigma / \sigma_c)^{\delta}\,(Sc)^{m}\,(\rho_L / \mu_L g)^{n}\,a_t \qquad (4.23)$$

$$k_V = C\,(Re_V)^{\alpha}\,(Sc_V)^{m}\,(a_t d_P)^{n}\,\left(\frac{RT}{a_t D_V}\right)^{\varepsilon} \qquad (4.24)$$

$$a_d/a_t \quad = \quad C\ (Re)^{\alpha}\ (We)^{\beta}\ (Fr)^{\gamma}\ (\sigma / \sigma_c)^{\delta} \qquad (4.25)$$

where Re, We, Fr and Sc are the Reynolds, Weber, Froude. and Schmidt number for liquid, Re_V and Sc_V are the Reynolds and Schmidt number for vapour and (σ / σ_c) is a wetting parameter.

Thus, with knowledge of the value of H_{OV} and the value of λ, using equation (4.19) the value of HETP can be estimated.