APPENDIX

1. **SAMPLE CALCULATIONS**

2. **COMPUTER PROGRAMS**

APPENDIX - 1

SAMPLE CALCULATIONS

A.1.1 SAMPLE CALCULATIONS FOR OBTAINING k_G FROM K_Ga :

For absorption of ammonia into water in a column packed with 0.025m carbon Raschig rings, ($a_t = 190\ m^2/m^3$, $\sigma_c = 56$ mN/m), under the conditions :-

$T = 26.6°C$, $L = 0.679\ kg/m^2s$, $G = 0.244\ kg/m^2s$, the value of K_Ga is reported as $2.76x10^{-2}\ kmol/m^3s$ atm. [From Table (5.5 A), observation (1)].

In order to estimate the dimensionless groups like Re, We Fr, etc. the relevant values of physical properties are the following :-

$\rho_L = 946.6\ kg/m^3$, $\mu_L = 0.867\ mNs/m^2$, $\sigma = 71.8$ mN/m,
$D_L = 2.43x10^{-9}\ m^2/s$, [From Table (8.2.1 A), observation (1)].

(i) <u>Estimation of different dimensionless numbers</u> :

Using the above data, the values of various dimensionless numbers work out to be as under :

$Re = (L/a_t\ \mu_L) = 4.122$ $We = (L^2/a_t \rho_L \sigma) = 3.39 \times 10^{-5}$
$Fr = (L^2\ a_t/\ \rho_L{}^2 g) = 8.99 \times 10^{-6}$ $(\sigma / \sigma_c) = 1.28$
$Sc = (\mu_L / \rho_L D_L) = 358.$

(ii) Estimation of k_La :

The generalised equation (4.2) could be used for obtaining the value of k_La. The values of constants C, α β γ δ , m and n to be utilised in equation (4.2) are 0.0833, 0.286, 0.22, 0.002, -0.442, - 0.5, and -0.333 respectively [From Table (8.1.2), Step (4)]. Therefore :

$$k_La = 0.0833\ [(Re)^{0.286}\ (We)^{0.22}\ (Fr)^{0.002}\ (\ \sigma\ /\ \sigma_c)^{-0.442}\ ]\ x$$
$$\ldots\ x\ [(Sc)^{-0.5}\ (\ \rho_L/\ \mu_L g)^{-0.333}\ a_t]$$
$$= 2.3416x10^{-3}\ s^{-1}.$$

(iii) Estimation of H :

For system ammonia - water, the values of the constants A and B to be utilised in equation (4.9) are 4425 and 10.82 respectively. Hence the value of M/P at 299.6°K works out to be as under :

$$ln(M/P) = (4425/T) - 10.82 = 2.9467.$$

Hence (M/P) = 51.766 (g mol/kg of solution)/atm.

or = $51.766x10^{-3}$ (kmol/kg of solution)/atm.

Since ρ_L = 996.6 kg/m^3,

Hence S_w = (M/P)$*\rho_L$ = 51.59 (k mol/m^3)/atm.

Hence, Henry's law constant for absorption of ammonia into water

$H = 1/S_w$ = 0.01938 atm/(k mol/m^3)

(iv) Estimation of k_Ga :

Using the value of $K_Ga = 2.767 \times 10^{-2}$ k mol/m^3s atm along with the value of $H = 0.01938$ atm/(k mol/m^3) and $k_La = 2.3416 \times 10^{-3}\ s^{-1}$ in equation (4.1), the value of k_Ga turns out to be = 3.5887×10^{-2} k mol/m^3s atm.

(v) Estimation of a :

For system ammonia - water, the effective interfacial area available for mass transfer is the dynamic area (a_{dy}). Therefore $a = a_{dy} = (a_w - a_{st})$. Hence, to obtain the values of 'a', the values of a_w and a_{st} are required.

(v-a) Estimation of a_w :

For obtaining the values of aw/at, the values of constants, C α β γ and δ to be utilised in equation (4.3) are 1.431, 0.0014, 0.165, 0.002, -0.442 respectively. [From Table (7.1.2), Step (12)].

$$a_w/a_t = 1.431\ (Re)^{0.0014}\ (We)^{0.165}\ (Fr)^{0.002}\ (\sigma / \sigma_c)^{-0.442}$$
$$= 0.2298.$$

Since $a_t = 190\ m^2/m^3$, therefore $a_w = 43.7\ m^2/m^3$.

(v-b) Estimation of a_{st} :

The value of static area under otherwise identical conditions are obtained by using the following generalised correlation [Table (7.4.3, Step (5)].

$$a_{st}/a_t = 0.1605\ (Re)^{0.1726}\ (Fr/We)^{0.5}\ (\sigma / \sigma_c)^{-0.725} = 0.0881$$

since $a_t = 190\ m^2/m^3$, therefore $a_{st} = 16.7\ m^2/m^3$. Thus, the area available for mass transfer, $a = a_w - a_{st} = 27\ m^2/m^3$.

(vi) Estimation of k_G :

Using the estimated values of k_Ga and 'a' as 3.5877×10^{-2} k mol/m^3s atm (step iv) and 27 m^2/m^3 (step v-b) respectively, the value of k_G works out to be 1.33×10^{-3} k mol/m^2s atm. Thus with the help of K_Ga data reported in Table (5.5 A) using the above mentioned "six steps procedure", the values of k_G have been estimated and are reported in Table (8.2.1 B).

A.1.2 SAMPLE CALCULATION FOR OBTAINING $k_L'a$ FROM K_Ga FOR ABSORPTION WITH CHEMICAL REACTION. (CO_2 - NaOH) :

For absorption of CO_2 into aqueous NaOH solutions, in a column packed with 0.0095 m ceramic Raschig rings, (a_t = 470 m^2/m^3 σ_C = 61 mN/m), under the conditions :-
T = 31°C, L = 2.79 kg/m^2s and G = 0.3831 kg/m^2s, the value of overall gas side mass transfer coefficient (K_Ga) for absorption with chemical reaction, is 15.6×10^{-2} k mol/m^3s atm. [From Table (5.7) observation (1)].

For estimation of dimensionless groups like, Re, We, Sc etc the relevant physical properties are the following :

ρ_L = 1061 kg/m^3, μ_L = 1.189 mNs/m^2 σ = 72.7 mN/m,
D_L = 1.161 kg/m^3, μ_G = 1.856×10^{-2} mNs/m^2 and
D_G = 1.6005×10^{-5} m^2/s. [From Table (8.4.1 A)].

(i) Estimation of various dimensionless numbers :

Using the above data the values of various numbers, work out to be:-

$Re = \{L/a_t \mu_L) = 4.9925 \qquad We = (L^2/a_t \rho_L \sigma) = 2.147x10^{-4}$

$Fr = (L^2 a_t/\rho_L{}^2 g) = 3.316x10^{-4} \qquad (\sigma/\sigma_C) = 1.1918$

$Re_G = (G/a_t \mu_G) = 43.91, \qquad Sc_G = (\mu_g/\rho_G D_G) = 0.768.$

(ii) Estimation of a_c :

Since for the system under consideration the gas absorption is accompanied by a chemical reaction following a second order kinetics, the area available for gas absorption should be evaluated by using equation (4.3) where the constants C, α , β , γ and δ are 0.455, 0.227, 0.058, 0.002, -1.104 respectively. [From Table (7.3.2) Step (10)].

$$a_c/a_t = 0.455\ Re^{0'227}\ We^{0.058}\ Fr^{0.002}\ (\sigma/\sigma_c)^{-1.104}$$
$$= 0.3255$$

Since $a_t = 470\ m^2/m^3$, therefore $a_c = 153.0\ m^2/m^3$.

(iii) Estimation of k_G :

The values of constants C, α , m and n for obtaining k_G using equation (4.6) are 1.75, 0.7, 0.4125 and -0.9 respectively [From Table (8.2.3), Step (3)]

$$k_G = 1.75\ Re_G^{0.7}\ Sc_G^{0.4125}\ (a_t\ d_p)^{-0.9}\ (RT/a_t D_G)^{-1}.$$
$$= 1.939x10^{-3}\ k\ mol/m^2\ s\ atm.$$

Since $a_c = 153\ m^2/m^3$, the value of $k_G a$ works out to be 0.2966 k mol/m^3 s atm.

(iv) Estimation of H :

Inlet concentration of NaOH = 1.8 k mol/m^3, assuming 20% change in concentration during the operation, the average concentration turns out to be (1.8 + 1.44)/2 = 1.62 k mol/m^3. The average concentration of Na_2CO_3 = (0 + 0.18)/2
= 0.09 k mol/m^3.

Barret's values of salting coefficients for ions and CO_2 at 31°C are [Data from Ref. (147)] :-

$h_{Na^+} = 0.091$, $h_{OH^-} = 0.066$, $h_{CO_3^=} = 0.021$ and $h_{CO_2} = 0.0218$

Since $h = h_+ + h_- + h_G$. Therefore for NaOH the value of h_1 turns out to be :- $h_1 = 0.091 + 0.066 - 0.0218 = 0.1352\ m^3/k$ mol.

and $I_1 = 0.5 \sum c_i Z_i^2 = 1.62$ k ion/m^3.

Similarly for Na_2CO_3, $h_2 = 0.0902$ and $I_2 = 0.27$ kion/m^3. substituting the values of h_1, I_1, etc in equation (4.10), the value of H'/H works out as under :

$$\log (H'/H) = h_1 I_1 + h_2 I_2 = (0.1352 \times 1.62)+(0.0902 \times 0.27)$$
$$= 0.2434$$

Therefore, (H'/H) = 1.75317.

The value of constants A and B for system CO_2 - water to be utilised in equation (4.7) for obtaining S_w are 1140 and 5.3 respectively.

Thus $\log (S_w) = (1140/T) - 5.3$,

Hence $S_w = 0.02818\ (k\ mol/m^3)/atm$

Hence, using equation (4.8) the value of H works out as 35.48 atm/(k mol/m^3). Therefore, the value of Henry's law constant for electrolyte solutions H' turns out to be 62.17 atm/(k mol/m^3).

(v) Estimation of $k_L^{'}a$:

Using the estimated values of k_Ga = 0.2966 k mol/m^3s atm step (iii), H' = 62.17 atm/(k mol/m^3) step (iv), the value of $k_L^{'}a$ using equation (4.5) works out as 1.0237 s^{-1}. Thus, with the help of K_Ga data reported in Table (5.7 A) using the above mentioned 'five-step procedure', the values of $k_L^{'}a$ have been estimated and are reported in Table (8.4.1. B).

A.1.3 SAMPLE CALCULATION FOR OBTAINING $k_L^{'}a$ FROM K_Ga FOR ABSORPTION WITH CHEMICAL REACTION (CO_2 - DEA System).

For absorption of CO_2 into aqueous Diethanolamine solutions in a column packed with 0.019 m stoneware Raschig rings, (a_t = 242 m^2/m^3, σ_c = 61 mN/m), under the conditions :-

T = 24°C, L = 1.329 kg/m^2s, G = 0.229 kg/m^2s, the value of overall gas side mass transfer coefficient (K_Ga) for absorption with chemical reaction, is K_Ga = 1.335x10^{-2} k mol/m^3s atm. [From Table (5.7) observation (112)].

For the estimation of dimensionless groups like Re, We, Sc etc., the relevant values of physical properties are the following :

ρ_L = 1010 kg/m^3, μ_L = 1.288 mNs/m^2,
σ = 60.2 mN/m, D_L = 1.276 x 10^{-9} m^2/s, ρ_G = 1.188 kg/m^3
μ_G = 1.827x10^{-2} mNs/m^2, D_G = 1.5993 x 10^{-5} m^2/s.
[from Table (8.4.1 A), data (112)].

(i) Estimation of various dimensionless numbers :

Using the above data the values of various numbers work out be as under :-

$Re = (L/a_t \mu_L) = 4.2637$ $\quad$ $We = (L^2/a_t \rho_L \sigma) = 1.2 \times 10^{-4}$

$Fr = (L^2 a_t / \rho_L^2 g) = 4.275 \times 10^{-5}$ $\quad$ $(\sigma / \sigma_c) = 0.987$

$Re_G = (G/a_t \mu_G) = 51.79$ $\quad$ $Sc_G = (\mu_G / \rho_G D_G) = 0.9616$

(ii) Estimation of a_c :

Since for the system under consideration gas absorption is accompanied by a chemical reaction following third order kinetics the area available for mass transfer during chemical absorption should be estimated by using equation (4.3) where constants C, α β γ and δ are 0.455, 0.227, 0.058, 0.002 & -1.104 respectively. [From Table (7.3.2), Step (10)].

$$a_c/a_t = 0.455\, Re^{0.227}\, We^{0.058}\, Fr^{0.002}\, (\sigma / \sigma_c)^{-1.104} = 0.3727$$

Since $a_t = 242\ m^2/m^3$, hence $a_c = 90.19\ m^2/m^3$.

(iii) Estimation of k_G :

The value of constants C, α , m, and n for obtaining k_G using equation (4.6) are 1.75, 0.7, 0.4125 and -0.9 respectively. [From Table (8.2.3), Step (3)].

$$k_G = 1.75\, Re_G^{0.7}\, Sc_g^{0.4125} (a_t D_P)^{-0.9}\, (RT/a_t D_G)^{-1}$$
$$= 1.0987 \times 10^{-3}\ k\ mol/m^2 s\ atm.$$

Since $a_c = 90.2\ m^2/m^3$, the value of $k_G a$ works out to be .0991 k mol/m^3s atm.

(iv) Estimation of Henry's Law constant for electrolyte solution H'

DEA is a non electrolyte. In order to estimate values H' for CO_2-DEA system, it could be assumed that the solubility of gas in liquid would be reduced to the same extent by DEA as by solution of ammonium bicarbonate with the same total Nitrogen content.

The concentration of DEA Solution = 0.99 k mol/m^3.
Inlet conversion of DEA = 28 %.
Exit convension of DEA = 45 %.
Average conversion of DEA = 36.5 %.
Hence mean concentration of carbamate
= 0.5 (avg. conversion of DEA) (DEA)
= 0.5 (0.365) (0.99) = 0.1806 $kion/m^3$

Onda's values of salting coefficients for ions and CO_2 at 24°C are:- $h_{NH_4^+} = -0.0737$, $h_{HCO_3^-} = 0.4286$, $h_G = -0.22715$ [Data for Ref (148)]. Thus, $h = (h_+ + h_- + h_G) = 0.12775$. Therefore $2 \times h = 0.2555$ and $I_1 = 0.1806$ $kion/m^3$.
Substituting the values of h_1, I_1 etc in equation (4.10) the value of H'/H works out as

$\log (H'/H) = h_1 I_1 = 0.0464$. Therefore $H'/H = 1.112$

In order the calculate H, initally the values of S_w are obtained utilising equation (4.7). The values ofconstants A and B in equation (4.7) for CO_2-water system are 1140 and 5.3 respectively.

Therefore, $\log S_w = (1140/T) - 5.3$.

Hence $S_w = 0.034545$ (k mol/m^3)/atm.

Using equation (4.8) the value of H works out as 28.947 atm/(k mol)/m^3); therefore the value of H' turns out to be 32.19 atm(k mol/m^3).

(v) Estimation of $K'_L a$:

Using the etimated values of $K_G a = 0.0991$ k mol/m^{3}s atm (step iii), and H' = 32.19 atm/(k mol/m^3), (step iv), the value of $k'_L a$ using equation (4.5) works out as 0.4356 s^{-1}. Thus, with the help of $K_G a$ data reported in Table (5.7 A) using the above mentioned 'five step procedure' the values of $k'_L a$ have been estimated and reported in Table (8.4.1 B)-observations (112-120).

A.1.4 SAMPLE CALCULATION FOR ESTIMATING H.E.T.P. :

For Ethylbenzene - Styrene distillation in a column packed with 0.15 m steel Raschig rings ($a_t = 330$ m^2/m^3 , $\sigma_C = 75$ mN/m) with L = 0.938 kg/m^{2}s and G = 0.932 kg/m^{2}s, the value of HETP is 0.271 m. The values of other relevant physical properties and parameters are as under :-

P = 0.131 atm a, T = 73.3 °C, $\sigma = 25.9$ mN/m^2, $\lambda = 0.933$,
$\rho_L = 822.9$ kg/m^3, $\mu_L = 0.39$ mNs/m^2,
$D_L = 3.569\text{x}10^{-9}$m^2/s, $\rho_V = 0.48$ kg/m^3, $\mu_V = 7.689\text{x}10^{-3}$ mNs/m^2, $D_V = 23.4 \times 10^{-6}$ m^2/s [From Table (9.1) and (9.2), observation (1)].

Other relevant information like liquid composition, relative volatility, column diameter and packed height is as follows :-

Liquid composition of key component (Ethylbenzene) = 58 mol %

relative volality, (α) = 1.37, Molecular weight of Ethylbenzene = 106.16 and Styrene = 104.14, column diameter = 0.5 m and packed height = 1.5 m. [Ref. (118)].

In order to calculate HETP, one requires knowledge of H_{OV} which in turn involves estimation of k_La, k^{-}_{V}, a and M_{avg}.

(i) Estimation of different dimensionless numbers :

Using the above data, the values of various numbers work out be as under .

$Re = (L/a_t\ \mu_L) = 7.288$ $\qquad Re_V = (G/a_t\ \rho_V) = 367.3$

$We = (L^2/a_t\ \rho_L\sigma) = 1.251 \times 10^{-4}$ $\qquad Sc_V = (\mu_V/\rho_V D_V) = 0.6845$

$Fr = (L^2 a_t/\rho_L^2 g) = 4.375 \times 10^{-5}$ $\qquad Sc_L = (\mu_L/\rho_L D_L) = 132.8$

$(\sigma/\sigma_c) = 0.3453.$

(ii) Estimation of k_La :

The generalised equation (4.24) could be used for obtaining the value of k_La. The valuesof constants-C, α, β, γ, δ, m and n to be utilised in equation (4.24) are 0.0833, 0.286, 0.22, 0.002, -0.442, -0.5 and -0.333 respectively [From Table (8.1.2), Step (4)].

$$k_La = 0.0833\ [(Re)^{0.286}\ (We)^{0.22}\ (Fr)^{0.002}\ (\sigma/\sigma_c)^{-0.442}]\ \times$$

$$\ldots \times [(Sc)^{-0.5}\ (\rho_L/\mu_L g)^{-0.333}\ a_t]$$

$$= 15.04 \times 10^{-3}\ s^{-1}.$$

(iii) Estimation of k_V :

The generalised equation (4.25) could be used for obtaining the value of k_V. The value of constants C, α, m and n to be utilised in equation (4.25) are 1.75, 0.7, 0.4125 and -0.9 respectively [From Table (8.2.3), Step (3)].

$$k_V = 1.75 \; (Re_V)^{0.7} \; (Sc_V)^{0.4125} \; (a_t D_P)^{-0.9} \; (RT/a_t \; D_V)^{-1}$$
$$= 6.0 \times 10^{-3} \text{ k mol/m}^2 \text{ s atm.}$$

(iv) <u>Estimation of a_d :</u>

The effective interfacial area available for mass transfer during distillation (a_d) is equivalent to the effective interfacial area available during physical absorption. The generalised equation (4.26) colud be used for obtaining the value of a_d/a_t. The value of constants C, α , β , γ , and δ to be utilised in equation (4.26) are 1.08, 0.099, 0.22, 0.002&-0.442, respectively. [From Table (7.2.2.) Step (10)].

$$a_d/a_t = 1.08 \; (Re)^{0.099} \; (We)^{0.22} \; (Fr)^{0.002} \; (\sigma / \sigma_c)^{-0.442} = 0.2854.$$

Since a_t = 330 m^2/m^3, therefore a_d = 94.182 m^2/m^3.

(v) <u>Estimation of M_{avg} :</u>

The average molecular weight of vapour can be obtained from knowledge of the vapour phase compositions. Since the values of liquid phase composition and relaive volatility are known, the vapour phase compositions can be estimated by the under mentioned expression, assuming that relative volability remains constant.

$$y_i = \frac{\alpha \; x_i}{1 + x_i \; (\; \alpha \; - 1)}$$

Since $x_{EB} = 0.58$ and $\alpha = 1.37$ therefore for $y_{EB} = 0.6542$ and $y_{styrene} = 0.3458$. The average molecular weight is then calculated by the expression $M_{avg} = y_1M_1 + y_2 M_2 = 105.46$.

(vi) <u>Estimation of H_L</u> :

Using the estimated value $k_La = 15.04 \times 10^{-3}\ s^{-1}$ (step ii), and the values of $L = 0.938\ kg/m^2s$ and $\rho_L = 822.9\ kg/m^3$, the value of H_L using equation (4.22) turns out to be 0.0757 m.

(vii) <u>Estimation of H_V</u> :

Using the estimated values of $K_V = 6 \times 10^{-3}$ k mol/m^{2}s atm (step iii), $a_d = 94.18\ m^2/m^3$ (step iv), $M_{avg} = 105.46$. (step v) with the values of $G = 0.932\ kg/m^2s$ and $P = 0.131$ atm, the value of H_G using the equation (4.23) works out to be 0.119 m.

(viii) <u>Estimation of H.E.T.P</u> :

Using the estimated values of $H_L = 0.0757$ m (step vi), $H_V = 0.119$ m (step vii) and the value of $\lambda = 0.933$, the value of H_{OV} using equation (4.21) works out as 0.189 m and substituting this value in equation (4.20), we obtain the value of HETP as 0.197 m.

Thus, with the help of preliminary data reported in Tables (9.1) and (9.2), using the above mentioned 'eight step procedure' the values of HETP have been estimated and are reported in Table (9.3).