Model Answers   MT-I (AS-4168)

Section A

(1)

(i) (a)   (ii) c   (iii) a   (iv) b   (v) a

(vi) d   (vii) b   (viii) d   (ix) b   (x) d

Section B

(3)

(i) Positive deviation from Raoult's law

A mixture whose total pressure is greater than that computed from ideality is said to show positive deviation from Raoult's law. Most mixture. fall in this category. In these case partial pressure of each component are larger than the ideal as shown in fig.
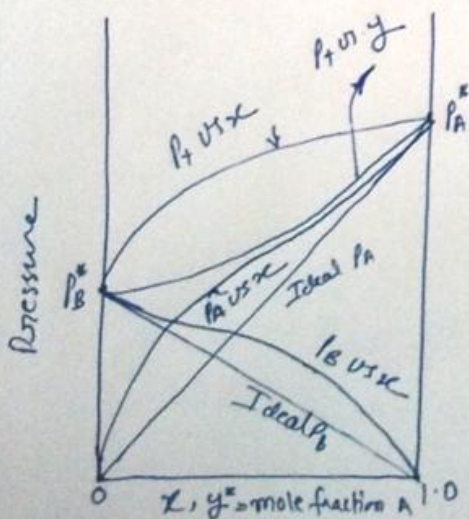

Fig. positive deviation from ideality

This is evidence that adhesive forces b/u different components (A-B) are weaker than the average cohesive forces b/u like components. dissimilarity of polarity or internal pressure will lead both components to escape the solution more easily so that its partial pressure is higher. It should be noted as the

concentration for each component approaches unity mole fraction, the partial pressures for that substance approach ideality tangentially. Raoult's law, in other words, is nearly applicable to the substance present in very large concentrations. This is the case for all substances except where association within the vapor or electrolytic dissociation within the liquid occurs.

Minimum-boiling mixtures—azeotropes When the positive deviations from ideality are sufficiently large and the vapor pressures of the two components are not too far apart, the total-pressure curves at constant temperature may rise through a maximum at some concentration, as in Fig. 9.7a. Such a mixture is said to form an *azeotrope*, or *constant-boiling mixture*. The significance of this is more readily seen by study of the constant-pressure section (Fig. 9.7b or c). The liquid- and vapor-composition curves are tangent at point L, the point of
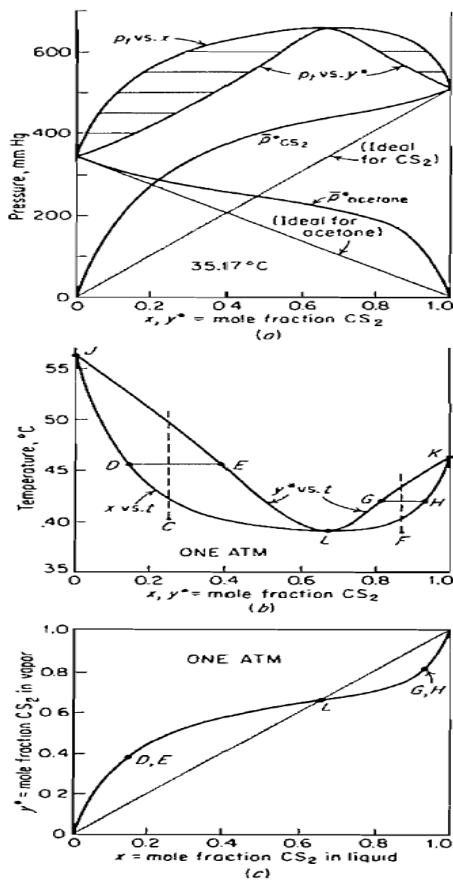

Figure 9.7 Minimum-boiling azeotropism in the system carbon disulfide—acetone: (a) at constant temperature; (b) and (c) at constant pressure.

azeotropism at this pressure, which represents the minimum-boiling temperature for this system. For all mixtures of composition less than L, such as those at C, the equilibrium vapor (E) is richer in the more volatile component than the liquid (D). For all mixtures richer than L, however, such as at F, the equilibrium vapor (G) is less rich in the more volatile substance than the liquid (H). A mixture of composition L gives rise to a vapor of composition identical with the liquid, and it consequently boils at constant temperature and without change in composition. If solutions either at D or H are boiled in an open vessel with continuous escape of the vapors, the temperature and composition of the residual liquids in each case move along the lower curve away from point L (toward K for a liquid at H, and toward J for one at D).

Solutions like these cannot be completely separated by ordinary distillation methods at this pressure, since at the azeotropic composition $y^* = x$ and $\alpha = 1.0$.† The azeotropic composition as well as its boiling point changes with pressure. In some cases, changing the pressure may eliminate azeotropism from the system.

Ans 3(ii)

Enthalpy-Concentration Diagrams

Binary vapor-liquid equilibria can also be plotted on coordinates of enthalpy vs. concentration at constant pressure. Liquid-solution enthalpies include both sensible heat and the heat of mixing the components

$$H_L = C_L(t_L - t_0)M_{av} + \Delta H_S \tag{9.10}$$

where C_L is the heat capacity of the solution, energy/(mol) (degree), and ΔH_S is the heat of solution at t_0 and the prevailing concentration referred to the pure liquid components, energy/mol *solution*. For saturated liquids, t_L is the bubble point corresponding to the liquid concentration at the prevailing pressure. Heat-of-solution data vary in form, and some adjustment of the units of tabulated data may be necessary. If heat is evolved on mixing, ΔH_S will be negative, and for ideal solutions it is zero. For ideal solutions, the heat capacity is the weighted average of those for the pure components.

For present purposes, saturated-vapor enthalpies can be calculated adequately by assuming that the unmixed liquids are heated separately as liquids to the gas temperature t_G (the dew point), each vaporized at this temperature, and the vapors mixed

$$H_G = y\left[C_{L,A}M_A(t_G - t_0) + \lambda_A M_A \right] + (1 - y)\left[C_{L,B}M_B(t_G - t_0) + \lambda_B M_B \right]$$
$$\tag{9.11}$$

where λ_A and λ_B are latent heats of vaporization of pure substances at t_G in energy per mole and $C_{L,A}$ and $C_{L,B}$ are heat capacities of pure liquids, energy/(mole)(degree).

In the upper part of Fig. 9.11, which represents a typical binary mixture, the enthalpies of saturated vapors at their dew points have been plotted vs. y and those of the saturated liquids at their bubble points vs. x. The vertical distances between the two curves at $x = 0$ and 1 represent, respectively, the molar latent heats of B and A. The heat required for complete vaporization of solution C is $H_D - H_C$ energy/mole solution. Equilibrium liquids and vapors may be joined by tie lines, of which line EF is typical. The relation between this equilibrium phase diagram and the xy plot is shown in the lower part of Fig. 9.11. Here the point G represents the tie line EF, located on the lower plot in the manner shown. Other tie lines, when projected to the xy plot, produce the complete equilibrium-distribution curve.

Figure 9.11 (with handwritten annotations)

(Adiabatic)
Pressure constant
mixture

H_G vs y

H_L vs x

tie-line

λ_B λ_A

0 x, y 1.0

1.0 y_F y 0 0 x_E x 1.0

Figure 9.11 Enthalpy-concentration coordinates.

Handwritten notes:

M > N, P will move closer to M

inverse lever arm rule

$\dfrac{M}{N} = \dfrac{\text{line } NP}{\text{line } PM}$

P = mixture (can be found by mass balance)

Remove N from sat vapour → sat liquid

similarly N is N mol of a mixture of properties H_N, z_N. Adiabatic mixing of M and N will produce P mol of a mixture of enthalpy H_P and concentration z_P. A total material balance is

$$M + N = P \tag{9.12}$$

and a balance for component A is

$$Mz_M + Nz_N = Pz_P \tag{9.13}$$

An enthalpy balance is

$$MH_M + NH_N = PH_P \tag{9.14}$$

Elimination of P between Eqs. (9.12) and (9.13) and between (9.12) and (9.14) yields

$$\frac{M}{N} = \frac{z_N - z_P}{z_P - z_M} = \frac{H_N - H_P}{H_P - H_M} \tag{9.15}$$

This is the equation of a straight line on the enthalpy-concentration plot, passing through points (H_M, z_M), (H_N, z_N), and (H_P, z_P). Point P is therefore on the straight line MN, located so that $M/N =$ line NP/line PM. Similarly if mixture N were *removed* adiabatically from mixture P, the mixture M would result.

Ans (4)

$$\log P_{MeOH} \text{ (mm Hg)} = 7.84863 - \frac{1473.11}{230 + t°c} \quad \text{①}$$

$$\log P_{EtOH} \text{ (mm Hg)} = 8.04494 - \frac{1554.3}{222.65 + t°c} \quad \text{②}$$

$$P_{MeOH} = P_A^*$$

$$P_{EtOH} = P_B^*$$

At boiling point of methanol & ethanol

$$P_A^* = 760 \text{ mm Hg}$$

$$P_B^* = 760 \text{ mm Hg}$$

Solving equation ①

$$t°c = 66.52°c \quad \text{(Boiling point of methanol)}$$

Solving equation ②

$$t°c = 78.32 \quad \text{(Boiling point of ethanol)}$$

From Raoult's law

$$P_A = P_A^* x$$

$$P_B = P_B^* (1-x)$$

$$P_T = P_A + P_B$$

$$P_T = P_A^* x + (1-x) P_B^*$$

$$x = \frac{P_\odot T - P_B}{P_A - P_B}$$

$$y = \frac{P_A}{P_T} = \frac{P_A^* x}{P_T}$$

At $\quad t = 66.52°c$

~~$x = 760$~~

$P_A^* = 760 \text{ mm Hz}$ $\qquad P_B^* = 467.6 \text{ mm Hz}$

At $\quad 78.32° c$

$P_A^* = 1262 \text{ mm Hz}$ $\qquad P_B^* = 760 \text{ mm Hz}$

Temp °C	Vapour pressure (mm Hz)	
θ	P_A^*	P_B^*
66.52°	760	467.6
68	880	498
72	1002	588
76	1160	698
78.32	1262	760

At $t = 65.52°C$

$$x = \frac{760 - 467.6}{760 - 467.6} = 1$$

$$y = \frac{760 \times 1}{760} = 1$$

In similar manner, values of x and y at other temperatures are calculated and tabulated as under

t°C	65.52	68	72	76	78.33
x	1	0.724	0.415	0.143	0
y	1	0.819	0.548	0.219	0
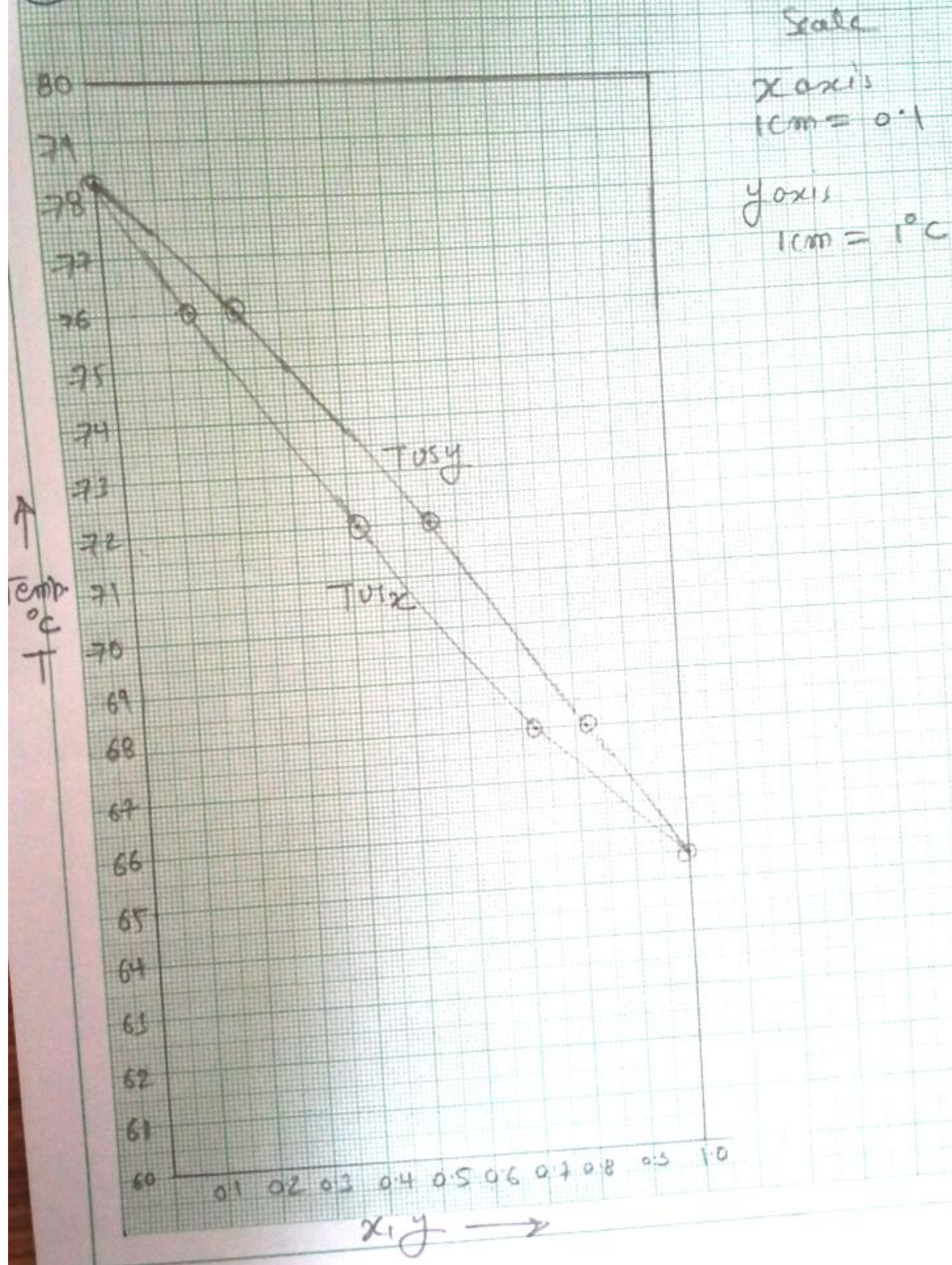
Scale
x axis 1 cm = 0.1
y axis 1 cm = 0.1
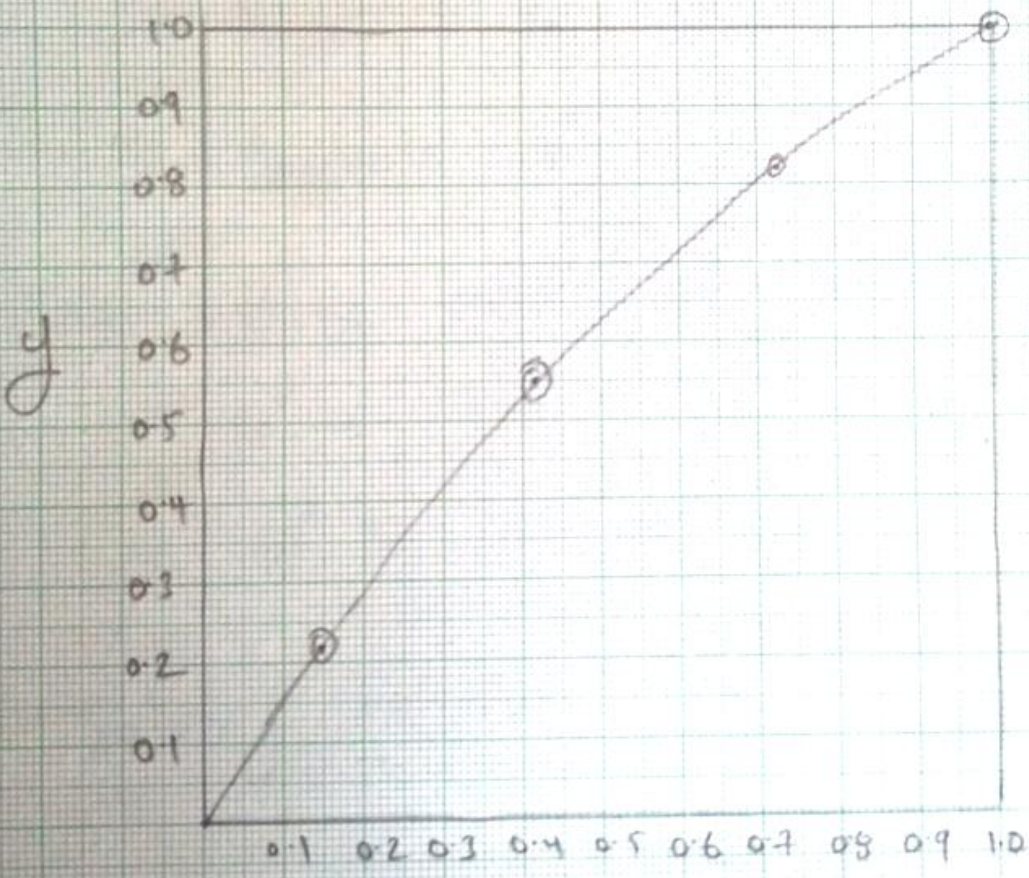
Ans (5)

(5) Given

$$x_F = 0.6$$

$$x_D = 0.9$$

$$x_B = 0.1$$

$$q = 1$$

$$R_D = 1.5 \, R_{om}$$

Murphree efficicory $= 0.6$

From graph $y_F' = 0.77$

$$R_{om} = (x_D - y_F') / (y_F' - x_F)$$

$$R_{om} = \frac{0.9 - 0.77}{0.77 - 0.6} = 0.76$$

Actual reflux ratio $= 1.5 \, R_{om}$

$$= 1.5 \times 0.76$$

$$= 1.14$$

$$\text{Intercept} = \frac{x_D}{R_D + 1} = \frac{0.9}{1.14 + 1} = 0.42$$

From graph.
   No of stages required $= 16$

Scale

X axis 1cm = 0·05
Y axis 1cm = 0·05

No of stages require = 16
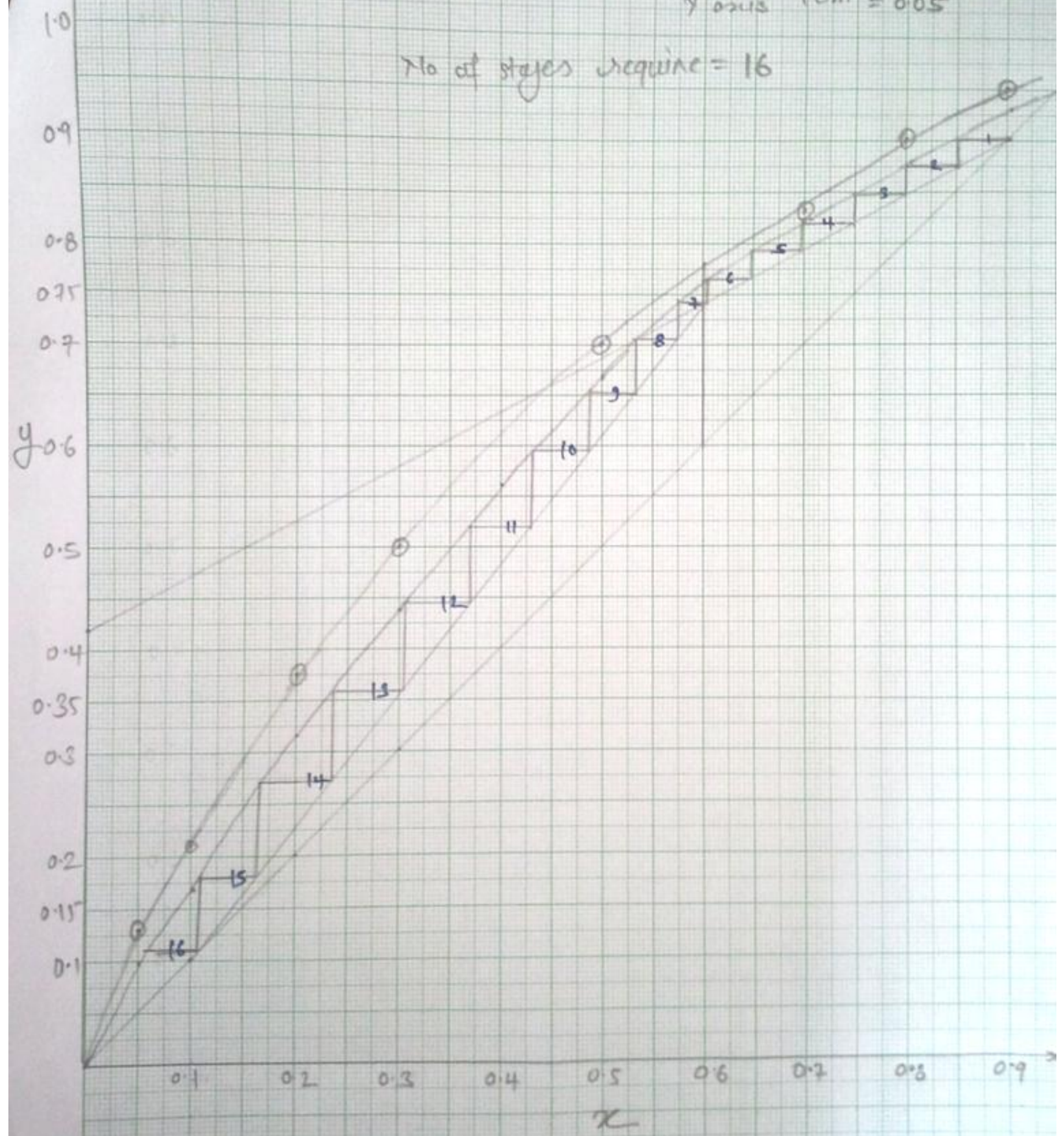
Ans (6)

(i)

OPTIMUM REFLUX RATIO. As the reflux ratio is increased from the minimum, the number of plates decreases, rapidly at first and then more and more slowly until, at total reflux, the number of plates is a minimum. It will be shown later that the cross-sectional area of a column usually is approximately proportional to the flow rate of vapor. As the reflux ratio increases, both V and L increase for a given production, and a point is reached where the increase in column diameter is more rapid than the decrease in the number of plates. The cost of the unit is
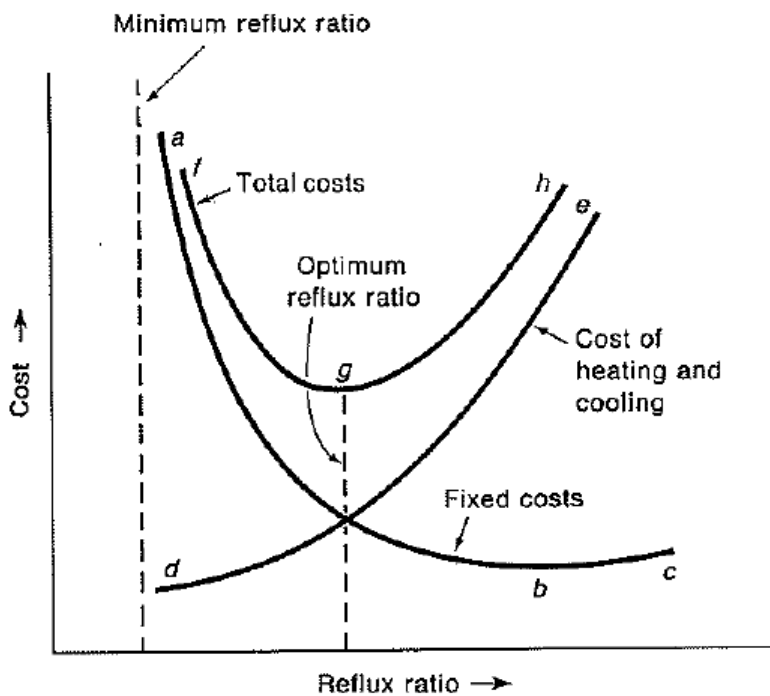
FIGURE 18.21
Optimum reflux ratio.

roughly proportional to the total plate area, that is, the number of plates times the cross-sectional area of the column, so the fixed charges for the column first decrease and then increase with reflux ratio. The cost of the heat exchange equipment—the reboiler and condenser—increases steadily with reflux ratio. This cost may be a small part of the total at low reflux ratios, but at high reflux ratios it becomes significant and contributes to the upturn in the curve for fixed charges (line *abc* in Fig. 18.21).

The reflux is made by supplying heat at the reboiler and withdrawing it at the condenser. The costs of both heating and cooling increase with reflux, as shown by curve *de* in Fig. 18.21. The total cost of operation is the sum of the fixed charges and the cost of heating and cooling, as shown by curve *fgh*. Curve *fgh* has a minimum at a definite reflux ratio not much greater than the minimum reflux. This is the point of most economical operation, and this reflux is called the *optimum reflux ratio*; it is usually in the range of 1.1 to 1.5 times the minimum reflux ratio. Actually, most plants are operated at reflux ratios somewhat above the optimum. The total cost is not very sensitive to reflux ratio in this range, and better operating flexibility is obtained if a reflux greater than the optimum is used.†
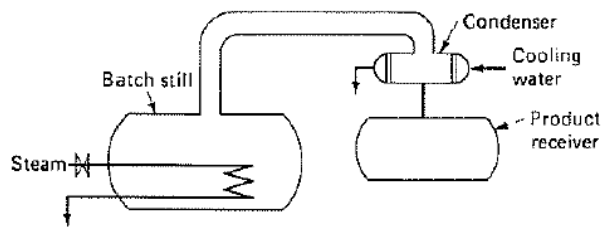
FIGURE 18.35
Simple distillation in a batch still.

BATCH DISTILLATION

In some small plants, volatile products are recovered from liquid solution by batch distillation. The mixture is charged to a still or reboiler, and heat is supplied through a coil or through the wall of the vessel to bring the liquid to the boiling point and then vaporize part of the batch. In the simplest method of operation, the vapors are taken directly from the still to a condenser, as shown in Fig. 18.35. The vapor leaving the still at any time is in equilibrium with the liquid in the still, but since the vapor is richer in the more volatile component, the compositions of liquid and vapor are not constant.

To show how the compositions change with time, consider what happens if n_0 moles are charged to a batch still. Let n be the moles of liquid left in the still at a given time and y and x be the vapor and liquid compositions. The total moles of component A left in the still n_A will be

$$n_A = xn \tag{18.72}$$

If a small amount of liquid dn is vaporized, the change in the moles of component A is $y\, dn$, or dn_A. Differentiating Eq. (18.72) gives

$$dn_A = d(xn) = n\, dx + x\, dn \tag{18.73}$$

Hence

$$n\, dx + x\, dn = y\, dn$$

By rearrangement,

$$\frac{dn}{n} = \frac{dx}{y - x} \tag{18.74}$$

Equation (18.74) is integrated between the limits of x_0 and x_1, the initial and final concentrations,

$$\int_{n_0}^{n_1} \frac{dn}{n} = \int_{x_0}^{x_1} \frac{dx}{y - x} = \ln\frac{n_1}{n_0} \tag{18.75}$$

Equation (18.75) is known as the Rayleigh equation. The function $dx/(y - x)$

Ans (7)

Fick's law:

An empirical relation for the diffusional molar flux, first postulated by Fick and, accordingly, often referred to as Fick's first law, defines the diffusion of component A in an isothermal, isobaric system. For diffusion in only the Z direction, the Fick's rate equation is

$$J_A = -D_{AB} \frac{dC_A}{dZ}$$

where D_{AB} is diffusivity or diffusion coefficient for component A diffusing through component B, and dC_A / dZ is the concentration gradient in the Z-direction.

Diffusivity of Co_2 in mixture

$$D_{1m} = \frac{1}{\dfrac{y_2{}'}{D_{12}} + \dfrac{y_3{}'}{D_{13}}}$$

where $y_2{}' = \dfrac{y_2}{y_2 + y_3} = \dfrac{0.15}{0.15 + 0.565} = 0.21$

$$y_3{}' = \frac{y_3}{y_2 + y_3} = \frac{0.565}{0.15 + 0.565} = 0.79$$

Therefore $D_{1m} = \dfrac{1*10^{-5}}{\dfrac{0.21}{1.54} + \dfrac{0.79}{1.62}}$

$$= 1.61*10^{-5} \ m^2/\text{sec}$$

Diffusivity of O_2 in the mixture,

$$D_{2m} = \frac{1}{\dfrac{y_1'}{D_{21}} + \dfrac{y_3'}{D_{23}}}$$

Where $y_1' = \dfrac{y_1}{y_1 + y_3} = \dfrac{0.285}{0.285 + 0.565} = 0.335$

(mole fraction on-2 free bans).

and

$$y_3' = \frac{y_3}{y_1 + y_3} = \frac{0.565}{0.285 + 0.565} = 0.665$$

and

$D_{21} = D_{12}$

Therefore

$$D_{2m} = \frac{1 * 10^{-5}}{\dfrac{0.335}{1.54} + \dfrac{0.665}{1.53}}$$

$$= 1.539 * 10^{-5} \ m^2/\text{sec}$$

Diffusivity of N_2 in the mixture

$$D_{3m} = \frac{1}{\dfrac{y_1'}{D_{31}} + \dfrac{y_2'}{D_{32}}}$$

where

$$y_1' = \frac{y_1}{y_1 + y_2} = \frac{0.285}{0.285 + 0.15} = 0.665$$

$$y_2' = \frac{y_2}{y_2 + y_1} = \frac{0.15}{0.15 + 0.285} = 0.335$$

$$D_{3m} = \frac{1*10^{-5}}{\dfrac{0.665}{1.62} + \dfrac{0.335}{1.53}}$$

$$= 1.588*10^{-5} \; m^2/\text{sec}$$

can be calculated, and is found to be, $D_{3m} = 1.588 * 10^{-5}$ m^2/sec.

Ans (8)

(i) $N_A = -CD_{AB} \dfrac{dy_A}{dz} + y_A(N_A + N_B)$

given: $N_B = -0.75\,N_A$

Therefore $N_A = -CD_{AB}\dfrac{dy_A}{dz} + y_A(N_A - 0.75\,N_A)$

$= -CD_{AB}\dfrac{dy_A}{dz} + 0.25\,y_A\,N_A$

$N_A - 0.25\,y_A\,N_A = -CD_{AB}\dfrac{dy_A}{dz}$

$N_A\,dz = -CD_{AB}\dfrac{dy_A}{1-0.25\,y_A}$

for constant N_A and C

$N_A \displaystyle\int_{Z_1}^{Z_2} dz = -CD_{AB}\int_{y_{A1}}^{y_{A2}} \dfrac{dy_A}{1-0.25\,y_A}$

$$\left[\int \dfrac{dx}{a+bx} = \dfrac{1}{b}\ln(a+bx) \right]$$

$N_A\,z = \left(-CD_{AB}\right)\left(\dfrac{-1}{0.25}\right)\left[\ln(1-0.25\,y_A)\right]_{y_{A1}}^{y_{A2}}$

$N_A = -\dfrac{4\,CD_{AB}}{z}\ln\left(\dfrac{1-0.25\,y_{A2}}{1-0.25\,y_{A1}}\right)$ ---------------------------------- (2)

Given:

$$C = \frac{p}{RT} = \frac{2 * 1.01325 * 10^5}{8314 * 273} = 0.0893 \; K\,mol/m^3$$

$$y_{A1} = \frac{p_{A1}}{P} = \frac{1.5}{2} = 0.75$$

$$y_{A2} = \frac{p_{A2}}{P} = \frac{0.5}{2} = 0.25$$

Substituting these in equation (2),

$$N_A = \frac{4 * 0.0893 * 0.275 * 10^{-4}}{0.2} \left[\ln \frac{1 - 0.25 * 0.25}{1 - 0.25 * 0.75} \right]$$

$$= 7.028 * 10^{-6} \; \frac{kmol}{m^2 \; sec}$$

Rate of diffusion = N_A S = 7.028 * 10^{-6} * π * $(0.5 * 10^{-2})^2$

$$= 5.52 * 10^{-10} \; kmol/sec$$

$$= 1.987 * 10^{-3} \; mol/hr.$$

(ii) $N_A = -CD_{AB} \dfrac{d\,y_A}{d\,z} + y_A \left(N_A + N_B\right)$

Given: $N_B = 0$

Therefore $N_A = -CD_{AB} \dfrac{d\,y_A}{d\,z} + y_A \; N_A$

$$N_A \int_{Z_1}^{Z_2} dz = -CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - y_A}$$

$$= \frac{CD_{AB}}{Z} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right)$$

$$= \frac{0.0893 * 0.275 * 10^{-4}}{0.2} \left[\ln\left(\frac{1 - 0.25}{1 - 0.75}\right)\right]$$

$$= 1.349 * 10^{-5} \frac{kmol}{m^2.\sec}$$

Rate of diffusion = $1.349\,8 \; 10^{-5} * \pi * (0.5 * 10^{-2})^2$

= 1.059 Kmol / sec

= 3.814 mol/hr

Ans (9)

(i)

Choice of Solvent for Absorption

If the principal purpose of the absorption operation is to produce a specific solution, as in the manufacture of hydrochloric acid, for example, the solvent is specified by the nature of the product. If the principal purpose is to remove some constituent from the gas, some choice is frequently possible. Water is, of course, the cheapest and most plentiful solvent, but the following properties are important considerations:

1. *Gas solubility*. The gas solubility should be high, thus increasing the rate of absorption and decreasing the quantity of solvent required. Generally solvents of a chemical nature similar to that of the solute to be absorbed will provide good solubility. Thus hydrocarbon oils, and not water, are used to remove benzene from coke-oven gas. For cases where the solutions formed are ideal, the solubility of the gas is the same in terms of mole fractions for all solvents. But it is greater in terms of weight fractions for solvents of low molecular weight, and smaller weights of such solvents, as measured in pounds, need to be used. A chemical reaction of solvent with the solute will frequently result in very high gas solubility, but if the solvent is to be recovered for reuse, the reaction must be reversible. For example, hydrogen sulfide can be removed from gas mixtures using ethanolamine solutions since the sulfide is readily absorbed at low temperatures and easily stripped at high temperatures. Caustic soda absorbs hydrogen sulfide excellently but will not release it in a stripping operation.

2. *Volatility*. The solvent should have a low vapor pressure since the gas leaving an absorption operation is ordinarily saturated with the solvent and much may thereby be lost. If necessary, a second, less volatile liquid can be used to recover the evaporated portion of the first, as in Fig. 8.3. This is sometimes done, for example, in the case of hydrocarbon absorbers, where a relatively

volatile solvent oil is used in the principal portion of the absorber because of the superior solubility characteristics and the volatilized solvent is recovered from the gas by a nonvolatile oil. Similarly, hydrogen sulfide can be absorbed by a water solution of sodium phenolate, but the desulfurized gas is further washed with water to recover the evaporated phenol.

3. *Corrosiveness*. The materials of construction required for the equipment should not be unusual or expensive.
4. *Cost*. The solvent should be inexpensive, so that losses are not costly, and should be readily available.
5. *Viscosity*. Low viscosity is preferred for reasons of rapid absorption rates, improved flooding characteristics in absorption towers, low pressure drops on pumping, and good heat-transfer characteristics.
6. *Miscellaneous*. The solvent if possible should be nontoxic, nonflammable, and chemically stable and should have a low freezing point.

(ii)

Two Film Theory

For steady-state mass transfer through a stagnant layer of fluid Eq. (21.19) or Eq. (21.24) can be used to predict the mass-transfer rate provided B_T is known. However, this is not a common situation, because in most mass-transfer operations turbulent flow is desired to increase the rate of transfer per unit area or to help disperse one fluid in another and create more interfacial area. Furthermore, mass transfer to a fluid interface is often of the unsteady-state type, with continuously changing concentration gradients and mass-transfer rates. In spite

of these differences, mass transfer in most cases is treated using the same type of equations, which feature a *mass-transfer coefficient k*. This coefficient is defined as the rate of mass transfer per unit area per unit concentration difference and is usually based on equal molal flows. The concentrations can be expressed in moles per volume or mole fractions, with subscript c indicating concentration and y or x mole fractions in the vapor or liquid phase:

$$k_c = \frac{J_A}{c_{Ai} - c_A} \tag{21.31}$$

or

$$k_y = \frac{J_A}{y_{Ai} - y_A} \tag{21.32}$$

Since k_c is a molar flux divided by a concentration difference, it has the units of velocity, such as centimeters per second or meters per second:

$$k_c = \frac{\text{mol}}{\text{s, cm}^2, \text{mol/cm}^3} = \text{cm/s}$$

For k_y or k_x the units are the same as for J_A, moles per area per time, since the mole fraction driving force is dimensionless. It is apparent that k_c and k_y are related by the molar density as follows:

$$k_y = k_c \rho_M = \frac{k_c P}{RT} \tag{21.33}$$

$$k_x = k_c \rho_M = \frac{k_c \rho_x}{M} \tag{21.34}$$

The significance of k_c is brought out by combining Eq. (21.31) with Eq. (21.20) for steady-state equimolal diffusion in a stagnant film. This gives

$$k_c = \frac{J_A}{c_{Ai} - c_A} = \frac{D_v(c_{Ai} - c_A)}{B_T} \frac{1}{c_{Ai} - c_A}$$

$$= \frac{D_v}{B_T} \tag{21.35}$$

Thus the coefficient k_c is the molecular diffusivity divided by the thickness of the stagnant layer. When dealing with unsteady-state diffusion or diffusion in flowing streams, Eq. (21.35) can still be used to give an effective film thickness from known values of k_c and D_v.

The basic concept of the *film theory* is that the resistance to diffusion can be considered equivalent to that in a stagnant film of a certain thickness.

Ans (10)

(10)

$$X_2 = 0$$
$$L_M \longrightarrow$$
$$G_M$$
$$Y_2 = 0.001$$

From material Balance

$$G_M(Y_1 - Y_2) = L_M(X_1 - X_2)$$

$$L_M \longleftarrow$$
$$G_M$$
$$X_2 = 0.08 \qquad Y_1 = 0.009$$

$$\frac{L_M}{G_M} = \frac{Y_1 - Y_2}{X_1 - X_2}$$

$$\frac{L_M}{G_M} = \left[\frac{0.009 - 0.001}{0.08 - 0}\right] = \frac{1}{10}$$
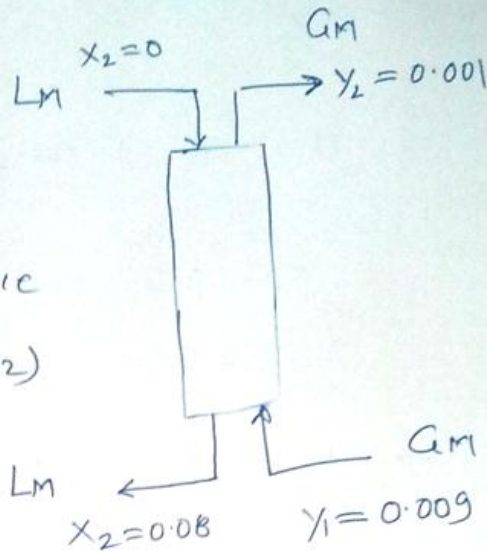
$$\frac{G_M}{L_M} = 10$$

$$NTU = \cfrac{Y_1 - Y_2}{\cfrac{(Y_1 - X_1^*) - (Y_2 - Y_2^*)}{\ln\left(\frac{Y_1 - Y_1^*}{Y_2 - Y_2^*}\right)}}$$

$$Y_1^* = 0.06\, X_1 = (0.06)(0.08) = 0.0048$$
$$Y_2^* = 0.06\, X_2 = (0.06)(0) = 0$$

$$NTU = \frac{0.009 - 0.001}{(0.009 - 0.0048) - (0.001 - 0)} \ln\left(\frac{0.009 - 0.0048}{0.001 - 0}\right)$$

$$= 3.587$$

$$HTU = H_y + m \frac{G_m}{L_m} H_x$$

$$= 0.36 + 0.06 \times 10 \times 0.24$$

$$= 0.504 \ m$$

Height of the packed section

$$Z_T = NTU \times HTU$$

$$= 3.587 \times 0.504$$

$$= 1.807 \ m$$

Ans (11)

(11)

Equilibrium isotherm data

$C \left(gm/cm^2 \right)$ 0.004   0.0087   0.019   0.027 0.094 0.195

$q \left(\dfrac{gm\ solute}{gm\ alumina} \right)$ 0.026   0.053   0.075   0.082   0.123   0.129

If the Langmuir isotherm fit the data then

$$\frac{1}{q} = m \cdot \frac{1}{C} + K$$

$1/q$ vs $1/C$ should be straight line with slope m and intercept K
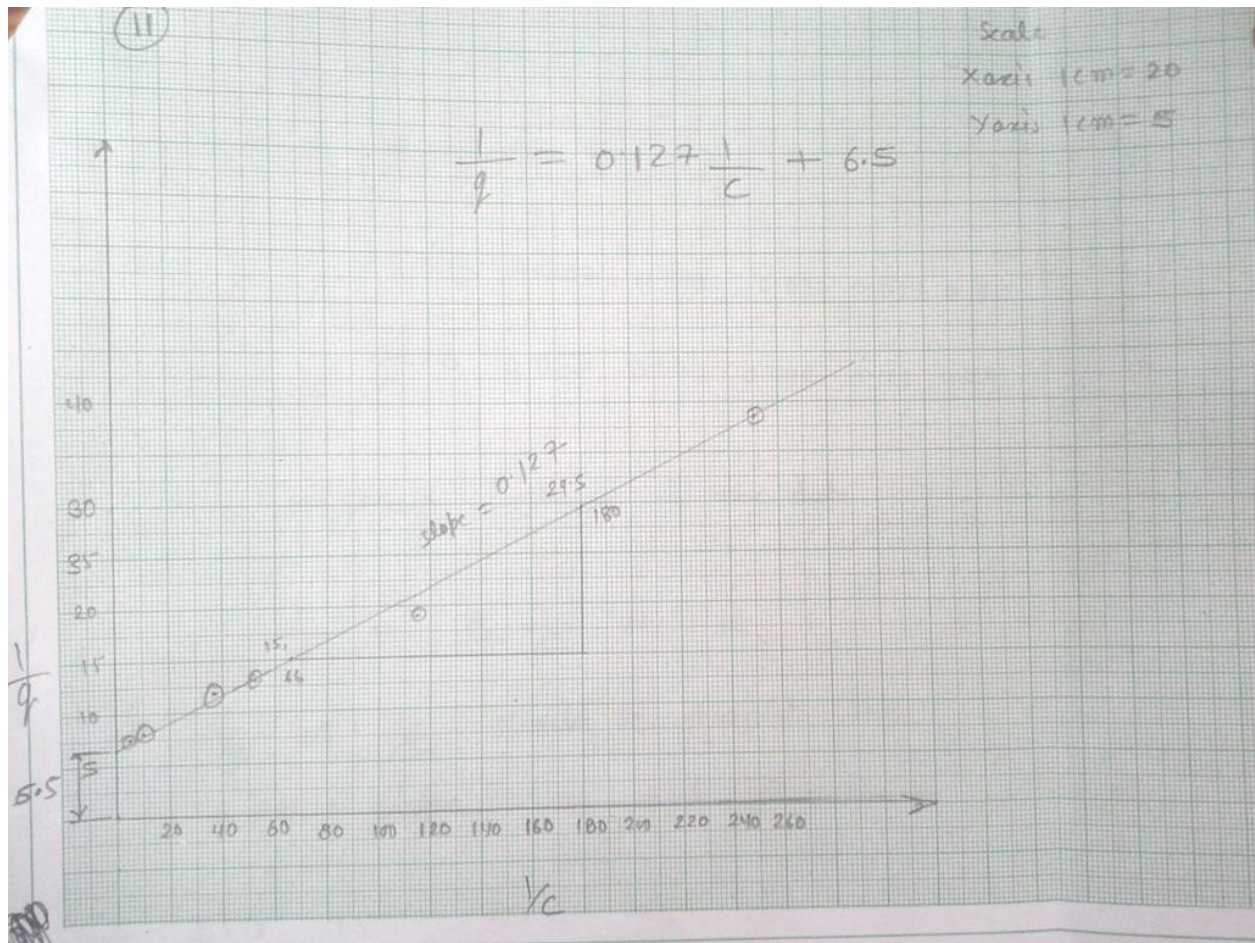
$\dfrac{1}{C}$ 250   115   52.6   37   10.6   5.1

$\dfrac{1}{q}$ 38.5   18.9   13.3   12.2   8.13   7.6

From graph it is clear that data fit fit the Langmuir isotherm with

$m = 0.127$
$K = 6.5$

$$\frac{1}{q} = 0.127 \frac{1}{c} + 6.5$$

Scale:
X axis 1 cm = 20
Y axis 1 cm = 5

slope = $\frac{0.127}{29.5}$

Ans (12)
(i) ELUTION

Desorption of the adsorbed solute by a solvent is called *elulion.* The desorption solvent is the *elutant,* and the effluent stream containing the desorbed solute and eluting solvent is the *eluate.* The *elulion curve* is a plot of the solute concentration in the eluate against quantity of eluate, as in Fig.. The initial rise in solute concentration of the eluate, *OA* in the figure, is found when the void spaces between the adsorbent particles are initially filled with fluid remaining from the adsorption. For liquids, if the bed is drained before elution, the elution curve starts at *A.* If elution is stopped after eluate corresponding to C has been withdrawn, the area under the curve *OABC* represents the quantity of solute desorbed. For a successful process, this must equal the

solute adsorbed during an adsorption cycle; otherwise solute will build up in the bed from one cycle to the next.
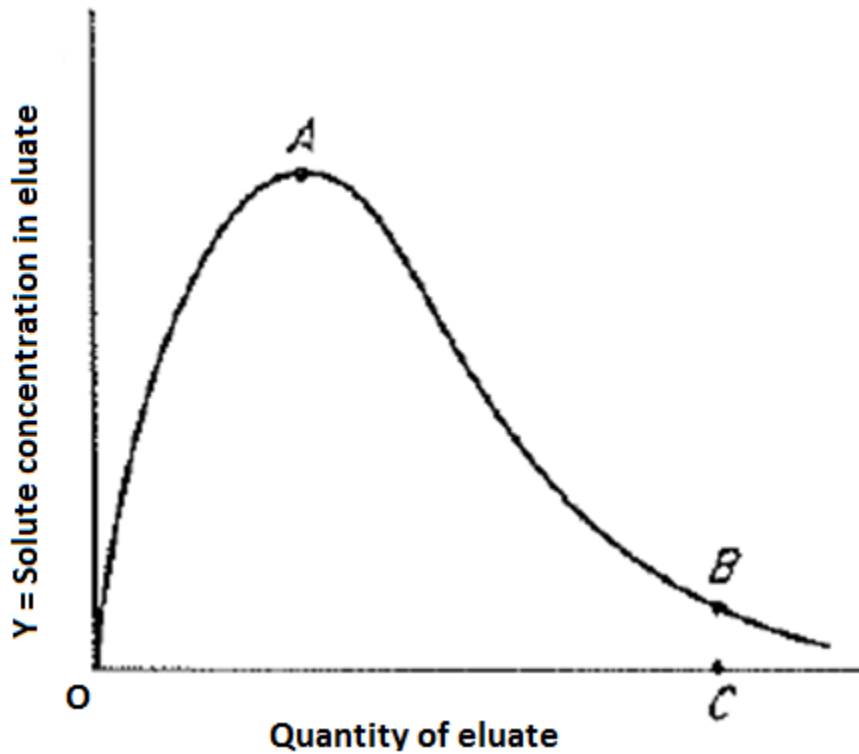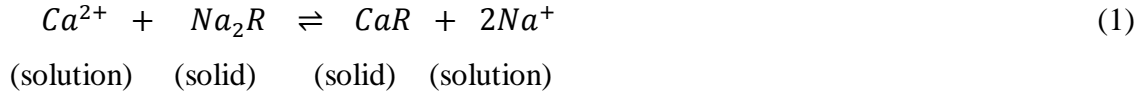

Figure. Elution of a fixed bed

(ii)ION-EXCHANGE PROCESSES

Introduction and Ion-Exchange Materials

Ion-exchange processes are basically chemical reactions between ions in solution and ions in an insoluble solid phase. The techniques used in ion exchange so closely resemble those used in adsorption that for the majority of engineering purposes ion exchange can be considered as a special case of adsorption.
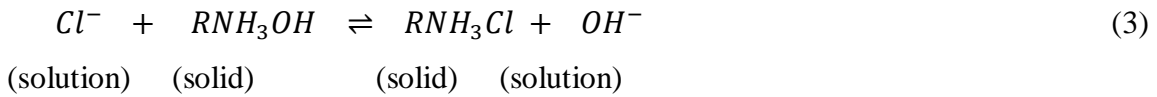
In ion exchange certain ions are removed by the ion-exchange solid. Since electroneutrality must be maintained, the solid releases replacement ions to the solution. The first ion-exchange materials were natural-occurring porous sands called zeolites and are cation exchangers. Positively charged ions in solution such as Ca^{2+} diffuse into the pores of the solid and exchange with the Na^+ ions in the mineral.

$$Ca^{2+} + Na_2R \rightleftharpoons CaR + 2Na^+ \tag{1}$$
$$\text{(solution)} \quad \text{(solid)} \quad \text{(solid)} \quad \text{(solution)}$$

where the R represents the solid. This is the basis for "softening" of water. To regenerate, a solution of NaCl is added which drives the reversible to reaction above the left. Almost all of these inorganic ion-exchange solids exchange only cations. Most present-day ion-exchange solids are synthetic resins or polymers. Certain synthetic polymeric resins contain sulfonic, carboxylic, or phenolic groups. These anionic groups can exchange cations.

$$Na^+ + HR \rightleftharpoons NaR + H^+ \tag{2}$$
$$\text{(solution)} \quad \text{(solid)} \quad \text{(solid)} \quad \text{(solution)}$$
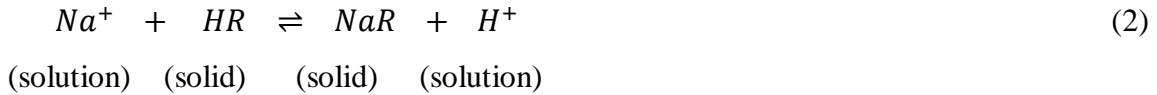
Here the R represents the solid resin. The Na^+ in the solid resin can be exchanged with H^+ or other cations. Similar synthetic resins containing amine groups can be used to exchange anions and OH⁻ in solution.

$$Cl^- + RNH_3OH \rightleftharpoons RNH_3Cl + OH^- \tag{3}$$
$$\text{(solution)} \quad \text{(solid)} \quad \text{(solid)} \quad \text{(solution)}$$

Equilibrium Relations in Ion Exchange

The ion-exchange isotherms have been developed using the law of mass action. For example, for the case of a simple ion-exchange reaction such as Eq. (2), HR and NaR represent the ion-exchange sites on the resin filled with a proton H^+ and a sodium ion Na^+. It is assumed that all of the fixed number of sites are filled with H^+ or Na^+. At equilibrium,

$$K = \frac{[NaR][H^+]}{[Na^+][HR]} \tag{4}$$

Since the total concentration of the ionic groups on the resin is fixed,

$$[\bar{R}] = constant = [NaR] + [HR] \tag{5}$$

Combining Eqs. (4) and (5),

$$[NaR] = \frac{K[\bar{R}][Na^+]}{[H^+] + K[Na^+]} \tag{6}$$

If the solution is buffered so **[H⁺]** is constant, the equation above for sodium exchange or adsorption is similar to the Langmuir isotherm.