12

ADSORPTION

12.1 INTRODUCTION

Adsorption operation involves contact of solids with either liquids or gases in which the mass transfer is towards solids. The reverse of this operation is called *Desorption*. Adsorption operations exploit the ability of certain solids to concentrate specific substances from fluid on to their surfaces. The adsorbed substance is called *adsorbate* and the solid substance is called *adsorbent*.

Typical applications of this solid–liquid operation are as follows:

- removal of moisture dissolved in gasoline
- de-colorization of petroleum products and sugar solutions
- removal of objectionable taste and odour from water.

The solid–gas operations include:

- dehumidification of air and gases
- removal of objectionable odours and impurities from gases
- recovery of valuable solvent vapours from dilute gas mixtures
- to fractionate mixtures of hydrocarbon gases such as methane, ethane and propane.

12.2 TYPES OF ADSORPTION

The two types of adsorption are *physical adsorption* or *physi-sorption* (van der Waals adsorption) and *chemi-sorption* (activated adsorption).

Physical adsorption is a readily reversible phenomenon, which results from the intermolecular forces of attraction between a solid and the substance adsorbed.

Chemi-sorption is the result of chemical interaction, generally stronger than physi-sorption between the solid and the adsorbed substance. This process is irreversible. It has importance in catalysis.

12.3 NATURE OF ADSORBENTS

Adsorbents are usually in granular form with their size ranging from 0.5 mm to 12 mm. They must neither offer high pressure drop nor get carried away by flowing stream. They must not loose their shape and size while handling. They must have larger surface area per unit mass and also lot of pores.

Some of the commonly used adsorbents, their sources and applications are given below:

Sl. No.	*Adsorbent*	*Source*	*Application*
1.	Fuller's earth	Naturally occurring clay is heated and dried to get a porous structure.	De-colorizing, drying of lubricating oils, kerosene and engine oils.
2.	Activated clay	Bentonite or other activated clay which are activated by treatment with sulfuric acid and further washing, drying and crushing.	Used for de-colorizing petroleum products.
3.	Bauxite	A naturally occurring hydrated alumina, activated by heating at 230–815°C.	Used for de-colorizing petroleum products and for drying gases.
4.	Alumina	A hard hydrated aluminium oxide, which is activated by heating to drive off the moisture and then crushed to desired size.	Used as desiccant.
5.	Bone-char	Obtained by destructive distillation of crushed bones at 600–900°C.	Used for refining sugar and can be reused after washing and burning.
6.	Activated carbon	(i) Vegetable matter is mixed with calcium chloride, carbonized and finally the inorganic compounds are leached away. (ii) Organic matter is mixed with porous pumice stones and then heated and carbonized to deposit the carbonaceous matter throughout the porous particle. (iii) Carbonizing substances like wood, sawdust, coconut shells, fruit pits, coal, lignite and subsequent activation with hot air steam. It is available in granular or pellated form.	De-colorizing of sugar solutions, chemicals, drugs, water purification, refining of vegetable and animal oils, recovery of gold and silver from cyanide ore-leach solution, recovery of solvent vapour from gas-mixtures, collection of gasoline hydro-carbons from natural gas, fractionation of hydrocarbon gases.

(Contd.)

(*Contd.*)

Sl. No.	*Adsorbent*	*Source*	*Application*
7.	Silica gel	A hard granular and porous product obtained from sodium silicate solution after treatment with acid. Normally has 4 to 7% water in the product.	Used for de-hydration of air and other gases, fractionation of hydrocarbons.
8.	Molecular sieves	These are porous synthetic zeolite crystals, metal alumino-silicates.	Dehydration of gases and liquids, and separation of gas–liquid hydrocarbon mixture.

12.4 ADSORPTION EQUILIBRIA

Different gases and vapours are adsorbed to different extent under comparable conditions as shown in Fig. 12.1.

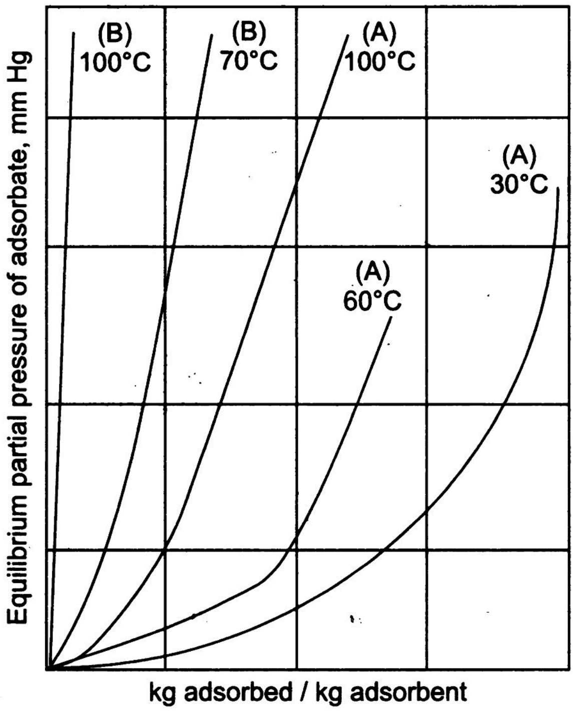


Fig. 12.1 Equilibrium adsorption on activated carbon.

As a general rule, vapours and gases with higher molecular weight and lower critical temperature are more readily adsorbed. To some extent, level of saturation also influences the degree of adsorption. The adsorption isotherms are generally concave to pressure axis. However, other shapes are also exhibited as shown in Fig. 12.2.

Repeated adsorption and desorption studies on a particular adsorbent will change the shape of isotherms due to gradual change in pore-structure. Further, adsorption is an exothermic process and hence the concentration of adsorbed gas

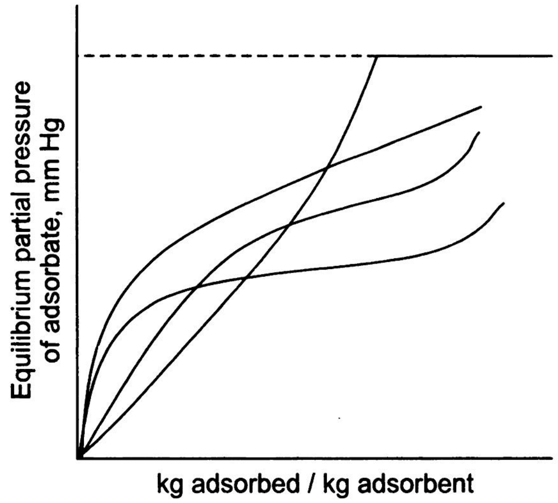


Fig. 12.2 Adsorption isotherms.

decreases with an increase in temperature at a constant pressure. Similarly an increase in pressure increases the concentration of adsorbed gas in the adsorbent at a constant temperature. There are three commonly used mathematical expressions to describe vapour adsorption equilibria, viz. Langmuir, Brunauer-Emmett-Teller (BET) and Freundlich isotherms. The first two are derived from theory whereas the last one is derived by a fit technique from the experimental data.

12.5 ADSORPTION HYSTERESIS

The adsorption and desorption operations exhibit different equilibrium phenomena as shown in Fig. 12.3 and is called adsorption hysteresis.

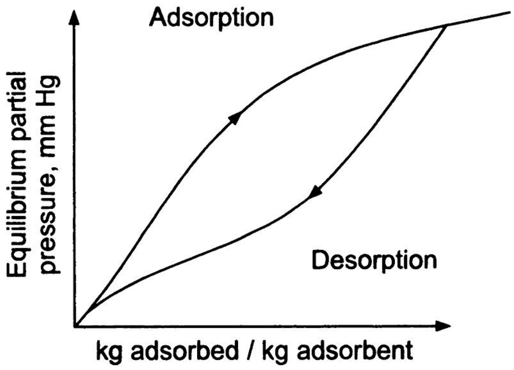


Fig. 12.3 Adsorption hysteresis.

This may be due to the shape of the openings to the capillaries and pores of the solid or due to the complex phenomena of wetting of the solid by the adsorbate. Whenever hysteresis is observed, the desorption curve is below the adsorption curve.

12.6 HEAT OF ADSORPTION

The differential heat of adsorption (–*H*) is defined as the heat liberated at constant temperature when unit quantity of vapour is adsorbed on a large quantity of solid already containing adsorbate. Solid so used is in such a large quantity that the adsorbate concentration remains unchanged.

The integral heat of adsorption, (ΔH) at any concentration X is defined as the enthalpy of the adsorbate–adsorbent combination minus the sum of the enthalpies of unit weight of pure solid adsorbent and sufficient pure adsorbed substance (before adsorption) to provide the required concentration X, at the same temperature.

The differential heat of adsorption and integral heat of adsorption are functions of temperature and adsorbate concentration.

12.7 EFFECT OF TEMPERATURE

Increase of temperature at constant pressure decreases the amount of solute adsorbed from a mixture. However, a generalization of the result is not easy. Figure 12.1 also indicates the effect of temperature.

12.8 EFFECT OF PRESSURE

Generally lowering of pressure reduces the amount of adsorbate adsorbed upon the adsorbent. However, the relative adsorption of paraffin hydrocarbon on carbon decreases at increased pressures.

12.9 LIQUIDS

The impurities are present both at low and high concentrations in liquids. These are normally removed by adsorption technique. The characteristics of adsorption of low and high concentration impurities are different. They are discussed below.

12.9.1 Adsorption of Solute from Dilute Solutions

Whenever a mixture of solute and solvent is adsorbed using an adsorbent, both the solvent and solute are adsorbed. Due to this, only relative or apparent adsorption of solute can alone be determined.

Hence, it is a normal practice to treat a known volume of solution of original concentration C_0, with a known weight of adsorbent. Let C^* be the final equilibrium concentration of solute in the solution.

If v is the volume of solution per unit mass of adsorbent (cc/g) and C_0 and C^* are the initial and equilibrium concentrations (g/cc) of the solute, then the apparent adsorption of solute per unit mass of adsorbent, neglecting any change in volume is $v(C_0 - C^*)$, (g/g). This expression is mainly applicable to dilute solutions. When the fraction of the original solvent which can be adsorbed is small, the C^* value depends on the temperature, nature and properties of adsorbent.

In the case of dilute solutions and over a small concentration range, *Freundich adsorption Isotherm* describes the adsorption phenomena,

$$C^* = K\,[v(C_0 - C^*)]^n \qquad (12.1)$$

Freundlich adsorption equation is also quite useful in cases where the actual identity of the solute is not known, e.g. removal of colouring substance from sugar solutions, oils etc. The colour content in the solution can easily be measured using spectrophotometer or colorimeter. The interpretation of this data is illustrated in worked example 2. If the value of n is high, say 2 to 10, adsorption is good. If it lies between 1 and 2, moderately difficult and less than 1 indicates poor adsorption characteristics. A typical adsorption isothermal for the adsorption of various adsorbates A, B and C in dilute solution at the same temperature for the same adsorbent is shown in Fig. 12.4.

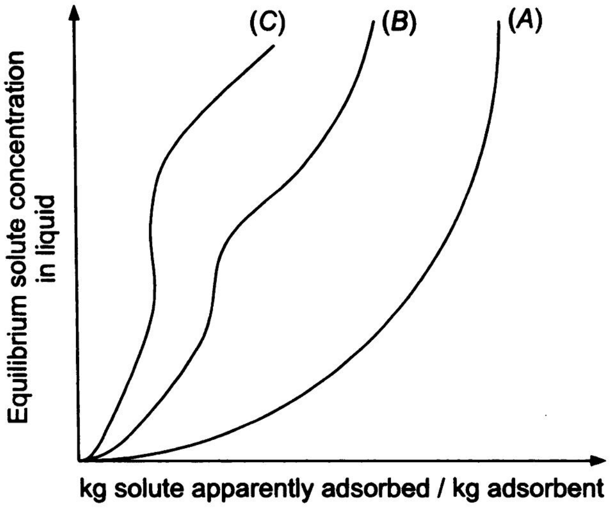


Fig. 12.4 Adsorption isotherms for various adsorbates.

12.9.2 Adsorption from Concentrated Solution

When the apparent adsorption of solute is determined over the entire range of concentrations from pure solvent (0% solute concentration) to pure solute (100% solute concentration), curves as shown in Fig. 12.5 will occur. Curve '1' occurs when the solute is more strongly adsorbed in comparison to solvent at all solute concentration. Whenever both solute and solvent are adsorbed to nearly the same extent, the 'S' shaped curve '2'occurs. In the range PQ solute is more strongly adsorbed than solvent. At point Q both are equally well adsorbed. In the range QR solvent is more strongly adsorbed.

12.9.3 Other Adsorption Isotherms

12.9.3.1 Langmuir adsorption isotherm

The theory proposed by *Langmuir* postulates that gases being adsorbed by a solid surface cannot form a layer more than a simple molecule in depth. His theory visualizes adsorption as a process consisting two opposite actions, a condensation of molecules from the gas phase on to the surface and an evaporation of molecules from the surface back into the body of the gas. When adsorption starts, every molecule colliding with the surface may condense on it. However, as adsorption

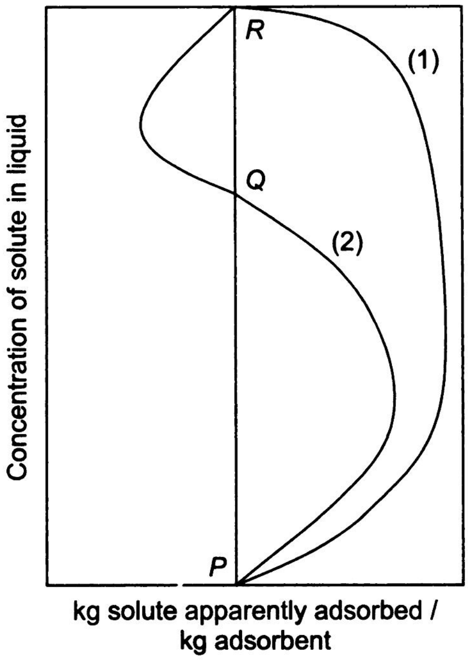


Fig. 12.5 Adsorption of solute in concentrated solutions.

proceeds, only those molecules which strike the uncovered area surface can be adsorbed. Due to this, the initial rate of condensation of molecules on the surface is very high and decreases as the time progresses. The molecules attached to the surface also get detached by factors like thermal agitation. The rate at which desorption occurs depends on the amount of surface covered by molecules and will increase as the surface becomes more fully saturated. When the rate of adsorption and desorption become equal, adsorption equilibrium is said to be reached. If 'θ' is the fraction of surface covered by adsorbed molecules at any instant, the fractional area available for adsorption is $(1 - \theta)$. The rate at which the molecules strike the unit area of surface is proportional to pressure.

Therefore the rate of condensation

$$= k_1(1 - \theta)P$$

where, k_1 is a constant.

Similarly, the rate of evaporation

$$\propto k_2\theta$$

where, k_2 is a constant.

Under adsorption equilibrium,

$$k_1(1 - \theta)P = k_2\theta$$

i.e.

$$\theta = \frac{k_1(1-\theta)P}{k_2 + k_1P}$$

$$= \frac{bP}{1+bP} \quad \text{where, } b = \frac{k_1}{k_2} \tag{12.2}$$

Now the gas adsorbed per unit area or unit mass of adsorbent, y, must obviously be proportional to the fraction of surface covered. Hence,

$$y = k\theta = k\left\{\frac{bP}{1+bP}\right\} = \frac{aP}{1+bP} \qquad (12.3)$$

where, a and b are constants. This is Langmuir adsorption Isotherm

12.9.3.2 BET adsorption isotherm

This postulates that the adsorption phenomenon involves the formation of many multilayers on the surface rather than a single one. Based on this, Brunauer, Emmett and Teller derived the following adsorption isotherm popularly known as BET adsorption isotherm.

$$\frac{P}{[V(P^o - P)]} = \frac{1}{[V_m C]} + \left[\frac{(C-1)}{V_m C}\right]\left[\frac{P}{P^o}\right] \qquad (12.4)$$

where, V is the volume, reduced to standard conditions of gas adsorbed at pressure P and temperature T, P° is the saturated vapour pressure of the adsorbate at temperature T, V_m is the volume of gas reduced to standard conditions, adsorbed when the surface is covered with a unimolecular layer, C is a constant at any given temperature given by exp $[(E_1 - E_2)/RT]$, where E_1 is the heat of adsorption for the first layer and E_2 is that for the second and higher layers.

12.10 TYPES OF OPERATION

Adsorption operations are carried out either on batch or continuous basis. Batch process is not very much used. However, a batch operation is quite useful in obtaining equilibrium data. Much widely used continuous operation can either be a single stage or a multistage operation. The multistage operation could once again either be a cross-current operation or a countercurrent operation.

12.10.1 Single Stage Operation

A schematic arrangement for a single stage operation is shown in Fig. 12.6.

The concentration of solute increases in the adsorbent from X_0 to X_1 (g/g) and the concentration of solute in the solution decreases from Y_0 to Y_1 (g/g).

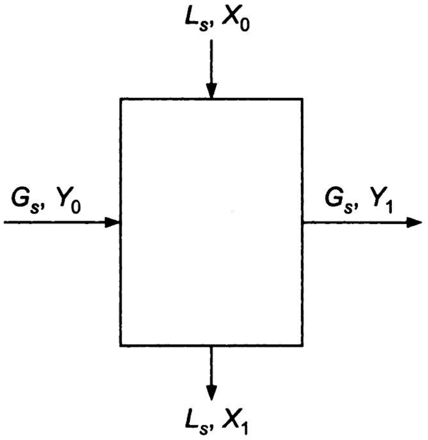


Fig. 12.6 Single stage operation.

The mass balance for solute gives

$$G_s\,[Y_0 - Y_1] = L_S\,[X_1 - X_0] \tag{12.5}$$

i.e.

$$-\frac{L_S}{G_S} = \frac{(Y_0 - Y_1)}{(X_0 - X_1)} \tag{12.6}$$

where (L_S/G_S) indicates the slope of the operating line passing through the points (X_0, Y_0) and (X_1, Y_1). If the leaving streams are in perfect equilibrium, then the point (X_1^*, Y_1^*) will lie on the equilibrium adsorption isotherm. If the equilibrium is not reached due to factors like poor contacting, then the point P represents the conditions of leaving streams as shown in Fig. 12.7.

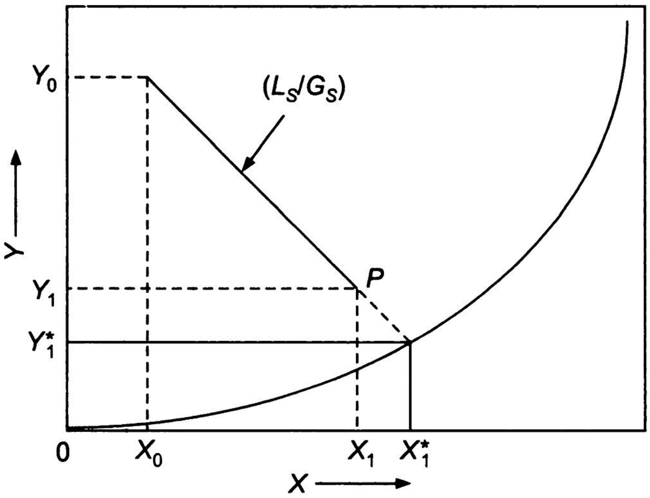


Fig. 12.7 Adsorption isotherm and operating line for a single stage operation.

Assuming the validity of Freundlich equation, especially when a low concentration of solute is involved, the equation can be written as

$$Y^* = mx^n \tag{12.7}$$

and at the final equilibrium conditions,

$$X_1 = \left(\frac{Y_1}{m}\right)^{1/n} \tag{12.8}$$

when the pure adsorbent is used, i.e. $X_0 = 0$.

Equation (12.8) yields

$$\frac{L_S}{G_S} = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} \tag{12.9}$$

12.10.2 Multistage Cross-current Operation

A schematic arrangement of multistage cross-current operation is shown in Fig. 12.8.

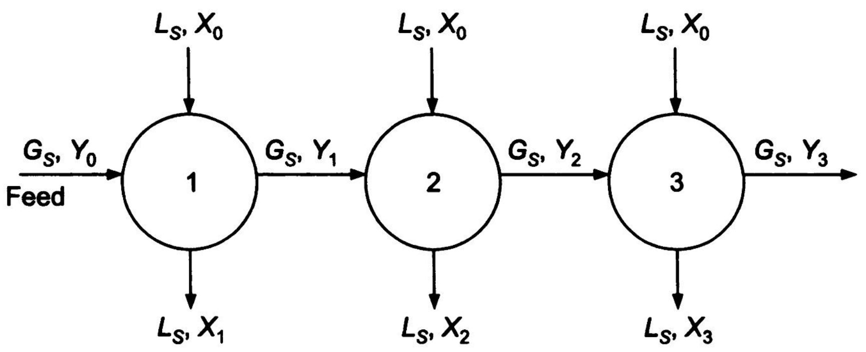


Fig. 12.8 Multistage cross-current operation.

Making a material balance of solute for stage 1 and use of Freundlich equation for the entry of pure adsorbent gives

$$G_S(Y_0 - Y_1) = L_{S1}(X_1 - X_0) \tag{12.10}$$

According to Eq. (12.9),

$$\frac{L_{S_1}}{G_S} = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} \tag{12.11}$$

A material balance of solute for stage 2 yields,

$$G_S(Y_1 - Y_2) = L_{S_2}(X_2 - X_0) \tag{12.12}$$

Use of Freundlich equation for the entry of pure adsorbent gives

$$\frac{L_{S_2}}{G_S} = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}} \tag{12.13}$$

A similar material balance for stage p yields

$$G_S(Y_{p-1} - Y_p) = L_{Sp}(X_p - X_0) \tag{12.14}$$

Using Freundlich equation as before gives

$$\frac{L_{Sp}}{G_S} = \frac{(Y_{p-1} - Y_p)}{\left(\frac{Y_p}{m}\right)^{1/n}} \tag{12.15}$$

This operation is represented graphically as shown in Fig. 12.9.

12.10.2.1 Steps involved in the determination of number of stages needed for a cross-current adsorption process

1. Draw the equilibrium curve (X vs Y).
2. Locate the point (X_0, Y_0) and draw the operating line with a slope ($-L_{S1}/G_S$).
3. The intersection of operating line and equilibrium curve yields (X_1, Y_1) – the conditions of stream leaving from stage I.

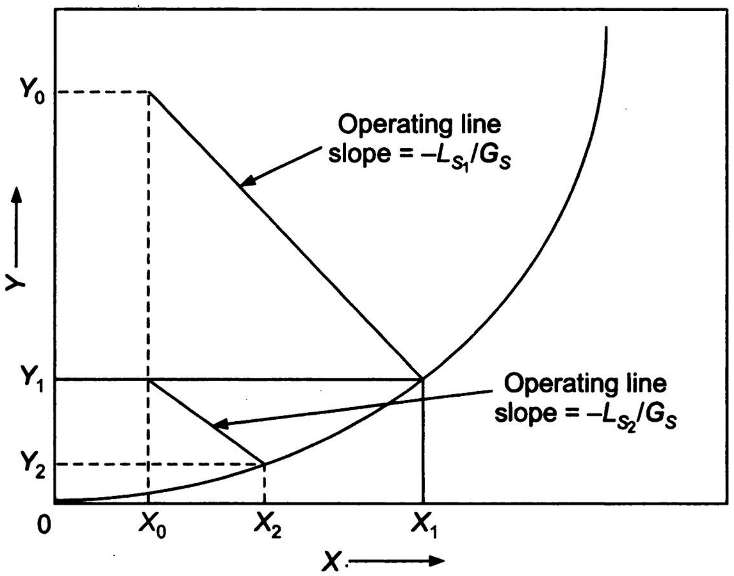


Fig. 12.9 Adsorption isotherm and operating line for a two-stage cross-current operation.

4. Locate (X_0, Y_1) and draw the operating line with a slope of ($-L_{S_2}/G_S$) (since X_0 remains constant for adsorbent for II stage).
5. Intersection of operating line and equilibrium curve yields (X_2, Y_2) — the conditions of leaving stream from stage II.
6. Proceed in the same way till the X_{Np} point is crossed and count the number of stages for the use of specified amount of adsorbent in each stage.

12.10.2.2 Optimisation of a two-stage cross-current operation

In a typical two-stage operation, the concentrations of solute both in the inlet solution stream and the outlet solution stream are fixed along with the feed rate of solution. The objective will be to use the minimum amount of adsorbent for this. If the quantity of the adsorbent is changed, the exit concentration of solution from each stage will also vary. However, the terminal conditions are always fixed and only the intermediate concentration is a variable. Hence, with one particular intermediate value, if the amounts of adsorbent used in both the stages are estimated, it will result in the minimum amount of adsorbent being used.

For the schematic arrangement shown in Fig. 12.10, the material balance equations for stages I and II are obtained from Eqs. (12.8) and (12.9) as

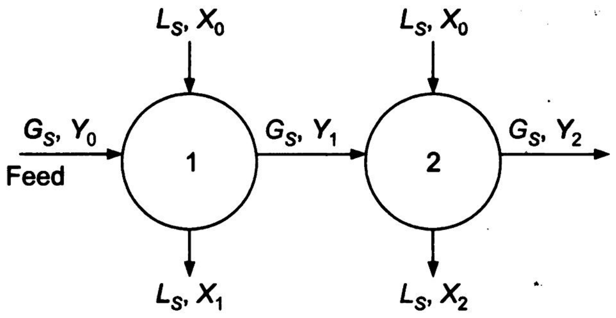


Fig. 12.10 Two-stage cross-current operation.

$$\frac{L_{S_1}}{G_S} = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}}$$

$$\frac{L_{S_2}}{G_S} = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}}$$

Adding Eqs. (12.11) and (12.12), we get

$$\left(\frac{L_{S_1} + L_{S_2}}{G_s}\right) = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} + \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}} \tag{12.16}$$

The total amount of adsorbent used can be optimised with respect to Y_1 (the intermediate concentration), the only variable on the R.H.S. of Eq. (12.16). The other parameters Y_0, Y_2, m and n are all fixed for a specified operation involving a specific adsorbent.

i.e.
$$\frac{d}{dY_1}\left[\frac{L_{S_1} + L_{S_2}}{G_S}\right] = \frac{d}{dY_1}\left[\frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} + \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}}\right] \tag{12.17}$$

$$= m^{1/n}\frac{d}{dY_1}\left[\frac{Y_0 - Y_1}{(Y_1)^{1/n}} + \frac{(Y_1 - Y_2)}{(Y_2)^{1/n}}\right]$$

i.e.
$$= m^{1/n}\frac{d}{dY_1}\left[\frac{(Y_0 - Y_1)Y_2^{1/n} + (Y_1 - Y_2)Y_1^{1/n}}{[(Y_2)^{1/n}(Y_1)^{1/n}]}\right]$$

$$m^{1/n}(Y_2)^{-1/n}\frac{d}{dY_1}\left[\frac{[(Y_0 Y_2^{1/n}) - (Y_1 Y_2^{1/n})] + [Y_1^{(1+1/n)} - Y_2 Y_1^{1/n}]}{Y_1^{1/n}}\right] \tag{12.18}$$

$$m^{1/n}(Y_2)^{-1/n}\frac{d}{dY_1}[Y_0 Y_2^{1/n} Y_1^{-1/n} - Y_2^{1/n} \cdot Y_1^{(1-1/n)} + Y_1 - Y_2] \tag{12.19}$$

$$m^{1/n}(Y_2)^{-1/n}\,[Y_0 \cdot Y_2^{1/n}\,(-1/n)Y_1^{-1-1/n} - Y_2^{1/n}(1 - 1/n)Y_1^{-1/n} + 1 - 0] \tag{12.20}$$

For minimum adsorbent R.H.S. of (12.20) should be zero.

i.e.
$$Y_0 Y_2^{1/n}(-1/n)Y_1^{-1-1/n} - (1 - 1/n)Y_2^{1/n}Y_1^{-1/n} + 1 - 0 = 0 \tag{12.21}$$

(since m, n and Y_2 have definite values)

Dividing by $\left(\frac{Y_2}{Y_1}\right)^{1/n}$, we get

$$\left(\frac{Y_0}{Y_1}\right)\left(\frac{-1}{n}\right) - \left(1 - \frac{1}{n}\right) + \left(\frac{Y_1}{Y_2}\right)^{1/n} = 0$$

i.e.
$$\left(\frac{Y_1}{Y_2}\right)^{1/n} - \left(\frac{1}{n}\right)\left(\frac{Y_0}{Y_1}\right) = 1 - \left(\frac{1}{n}\right) \tag{12.22}$$

Equation (12.22) can be solved by trial and error to get the intermediate concentration Y_1 which will optimise the total quantity of adsorbent to be used. However, also using the chart as shown in Fig. 12.11, we can get the intermediate concentration.

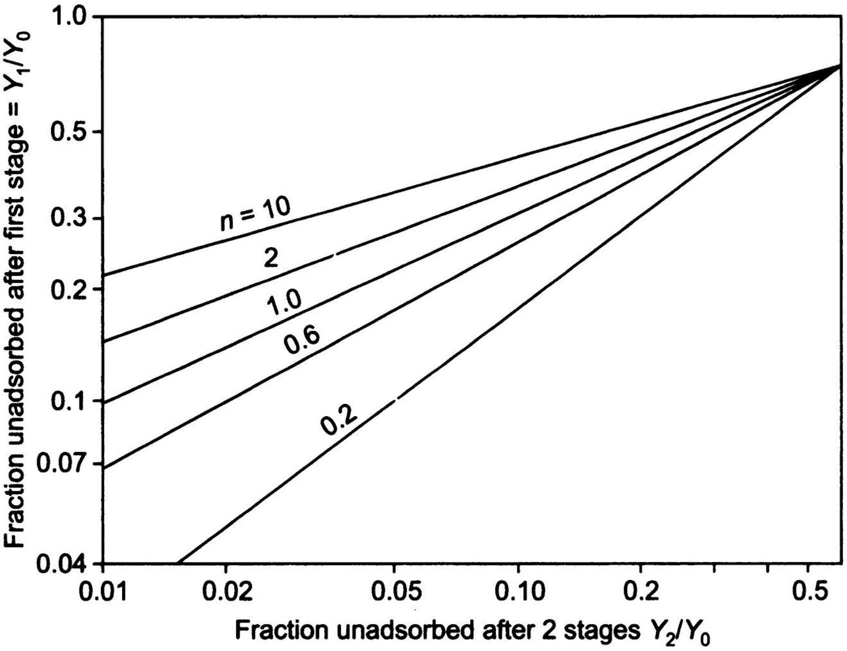


Fig. 12.11 Minimum total adsorbent two-stage cross-current Eq. (12.22).

12.10.3 Multistage Countercurrent Adsorption

The schematic arrangement as shown in Fig. 12.12 represents a multistage countercurrent operation.

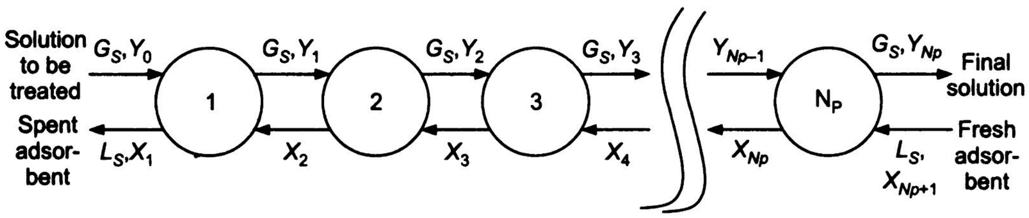


Fig. 12.12 Multistage countercurrent operation.

Solute balance for the system as a whole gives

$$G_S(Y_0 - Y_{Np}) = L_S(X_1 - X_{N_p+1}) \tag{12.23}$$

i.e.
$$\left(\frac{L_S}{G_S}\right) = \frac{(Y_0 - Y_{Np})}{(X_1 - X_{Np+1})} \tag{12.24}$$

Equation (12.24) gives the slope of the operating line passing through the terminal conditions (X_1, Y_0) and (X_{Np+1}, Y_{Np}). By conventional stepwise construction starting from the point (X_1, Y_0), the number of theoretical stages are estimated. This operation is represented graphically as shown in Fig. 12.13.

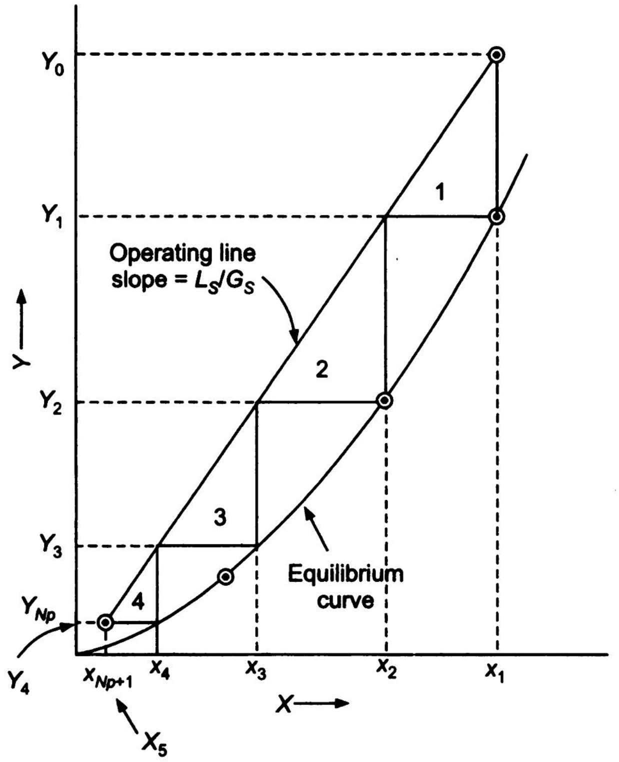
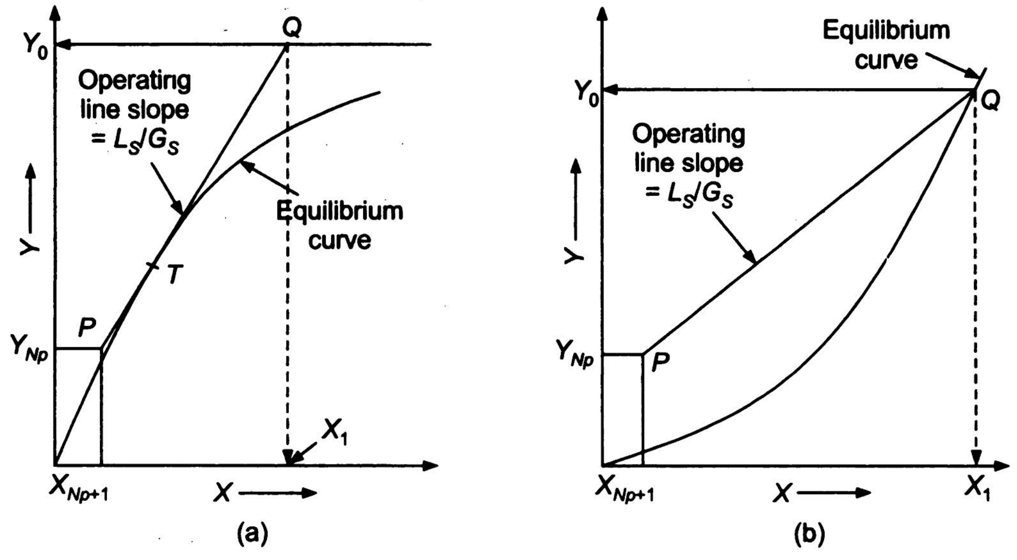


Fig. 12.13 Countercurrent multistage adsorption.

In order to determine the minimum amount of adsorbent for the process, draw a line from the point P (X_{Np+1}, Y_{Np}) which could be a tangent to the equilibrium curve. In such cases, the slope of the line gives the ratio of $(L_S/G_S)_{\min}$. However, in the case of equilibrium curve being a straight line or concave upwards, draw a horizontal line from Y_0 to intersect the equilibrium curve, (or line) at a point by Q and then join PQ which gives the slope of the operating line $(L_S/G_S)_{\min}$. The above two cases have been shown graphically in Figs. 12.14(a) and 12.14(b) respectively.



(a) (b)

Fig. 12.14 Operating line and minimum adsorbent/solvent ratio for infinite stages.

12.10.3.1 Steps involved in determining the number of stages in a multistage countercurrent operation

1. Draw the equilibrium curve.
2. Locate the point P (X_{Np+1}, Y_{Np}).
3. Draw a line with a slope of (L_S/G_S), where L_S is the mass flow rate of solute free adsorbent and G_S is the mass flow rate of solution on solute free basis.
4. Starting from (X_1, Y_0) by stepwise construction, estimate the number of stages till the point (X_{Np+1}, Y_{Np}) is crossed. The operation is graphically shown in Fig. 12.14.
5. If it is desired to determine the amount of adsorbent needed for a specified level of solute removal from a solution stream with a specified number of stages, draw the operating line of different slopes by trial and error and choose the one which gives exactly the same number of specified stages and the specified concentration in the liquid stream. From the slope of the operating line, thus chosen, determine the amount of adsorbent to be used and the solute concentration in the adsorbent.

12.10.3.2 Optimization of two-stage countercurrent adsorption

A typical two-stage countercurrent operation is shown schematically in Fig. 12.15.

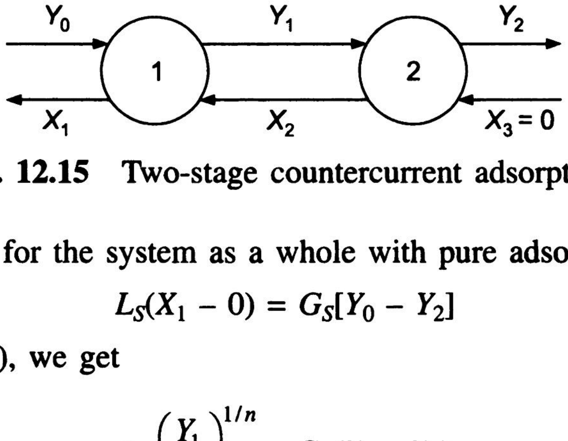


Fig. 12.15 Two-stage countercurrent adsorption.

Solute balance for the system as a whole with pure adsorbent yields

$$L_S(X_1 - 0) = G_S[Y_0 - Y_2] \tag{12.25}$$

Applying Eq. (12.8), we get

$$L_S\left(\frac{Y_1}{m}\right)^{1/n} = G_S(Y_0 - Y_2) \tag{12.26}$$

$$\frac{L_S}{G_S} = \frac{(Y_0 - Y_2)}{\left(\frac{Y_1}{m}\right)^{1/n}} \tag{12.27}$$

Applying a similar balance for stage 2, we get

$$G_S(Y_1 - Y_2) = L_S(X_2 - 0) = L_S\left(\frac{Y_2}{m}\right)^{1/n} \tag{12.28}$$

$$\left(\frac{L_S}{G_S}\right) = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}} \tag{12.29}$$

Equating Eqs. (12.27) and (12.29), we get

$$\frac{(Y_0 - Y_2)}{\left(\frac{Y_1}{m}\right)^{1/n}} = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}}$$

$$\frac{(Y_0 - Y_2)}{Y_2} = \frac{(Y_1 - Y_2)}{Y_2}\left[\left(\frac{Y_1}{m}\right)^{1/n} \times \left(\frac{Y_2}{m}\right)^{-1/n}\right]$$

$$\left(\frac{Y_0}{Y_2}\right) - 1 = \left(\frac{Y_1}{Y_2}\right)^{1/n}\left[\left(\frac{Y_1}{Y_2}\right) - 1\right] \tag{12.30}$$

Since Y_0, Y_2, n are all specific values for a specified level of adsorption and also a specific adsorbent, the only unknown Y_1, can be estimated by trial and error. Alternately, Y_1, can be estimated by the following chart as shown in Fig. 12.16.

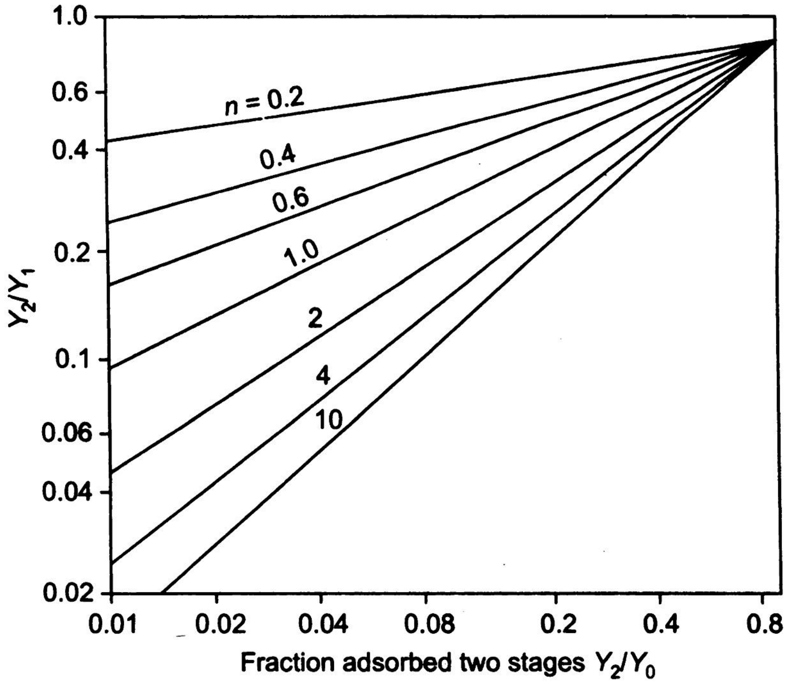


Fig. 12.16 Two-stage countercurrent adsorption Eq. (12.27).

12.11 CONTINUOUS ADSORPTION

In these adsorbers, the fluid and adsorbent are in continuous contact without any separation of the phases. This is quite analogous to gas absorption with the solid adsorbent replacing the liquid solvent. The operation can be carried out in strictly continuous, steady state fashion with both fluid and solid moving at constant rate and the composition remains constant at a particular point. It can also be operated on semi-continuous basis with solid particles remaining stationary and fluid in moving condition. Such operations constitute unsteady adsorption process.

12.11.1 Steady State Adsorption

Continuous differential contact tower is schematically represented in Fig. 12.17.

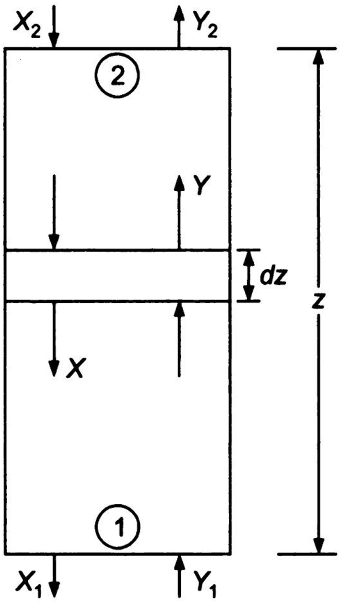


Fig. 12.17 Continuous differential contact tower.

Solute balance for the entire tower is

$$G_S(Y_1 - Y_2) = L_S(X_1 - X_2) \tag{12.31}$$

Solute balance for the upper part of the tower is

$$G_S(Y - Y_2) = L_S(X - X_2) \tag{12.32}$$

Using Eq. (12.31), one can draw the operating line and Eq. (12.32) gives us the concentration of the two phases at any point in the tower.

Making a solute balance across the element of thickness dZ,

$$L_S\,(dX) = G_S\,dY = K_ya\,(Y - Y^*)\,dZ \tag{12.33}$$

where K_y a is mass transfer coefficient based on the outside surface area a of particles, kg/m^3.s.(ΔY) and Y^* is the equilibrium concentration of the fluid corresponding to its concentration X.

Equation (12.33) on integration yields

$$N_{toG} = \int_{Y_2}^{Y_2} \frac{dY}{(Y - Y^*)} = \frac{K_ya}{G_S}\int_0^Z dZ = \frac{Z}{H_{toG}} \tag{12.34}$$

where $H_{toG} = G_S/K_ya$

N_{toG} can be determined graphically as usual.

12.11.2 Unsteady State Adsorbers

When a fluid mixture is passed through a stationary bed of adsorbent, the adsorbent adsorbs solute continuously and it results in an unsteady state operation. Ultimately, the bed may get saturated and no further adsorption results. The change in concentration of effluent stream is shown in Fig. 12.18. The system indicates an exit concentration varying from C, to a final concentration very close to inlet concentration. The point *A* indicates break point. The portion from *A* to *B* is termed the break through curve. Beyond this, very little adsorption takes place, indicating that the system has more or less reached equilibrium or saturation.

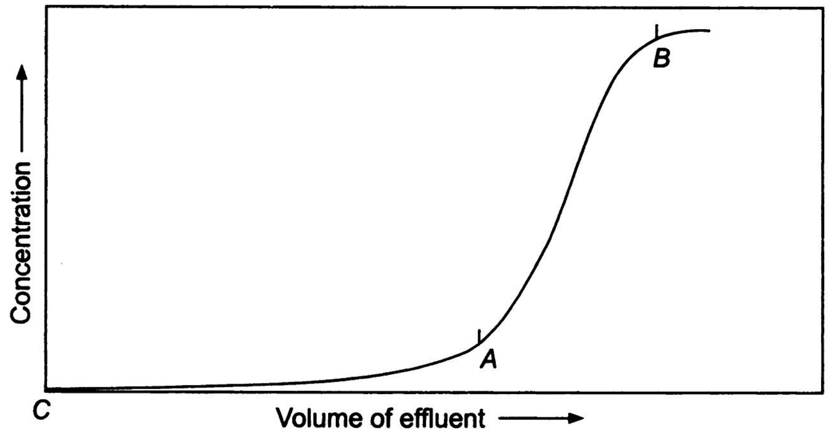


Fig. 12.18 The adsorption wave.

12.12 EQUIPMENT FOR ADSORPTION

Equipment are available for adsorption of a solute from a gaseous or a liquid stream. When the solute (which could be colouring matter, odorous substances, valuable solutes etc.) is strongly adsorbed from a liquid stream, one can use contact filtration equipment which can be operated as batch units, semi-continuous or as continuous ones. Continuous ones can be realized by fluidized bed techniques. These are similar to mixer-settler units used in extraction operations. Generally gases are treated with fluidized bed techniques.

12.12.1 Contact Filtration Equipment

The equipment consists of a mixing tank in which the liquid to be treated and the adsorbent are thoroughly mixed at the operating temperature and for a specified duration of time. In some cases like ion exchange sparging is done with air. Subsequently the slurry is filtered off to separate the solids from the solution. The filtration is done in a filter press or centrifuge or in a continuous rotary filter. Multi stage operations could easily be done by providing a number of tanks and filter combinations. The filter cake is usually washed to displace the solution. If the adsorbate is the desired product, then it can be desorbed by contact with a solvent other than the one which constituted the solution and the one in which the solute is more readily soluble. When the solute is more volatile, it can be removed by the passage of steam or warm air through the solid. Whenever the adsorbent is activated carbon, care must be taken so that the adsorbent does not burn away at high temperatures of desorption operation. Adsorbent can also be regenerated by burning away the adsorbate.

12.12.2 Fluidised Beds

When a mixtures of gases are to be treated on a continuous basis, it is preferable to use fluidized beds. This is done by passing the gases at high velocities through a bed of granular solids in which the adsorption occurs. The beds of solids remain in suspended condition throughout the operation. The bed can be regenerated by passing steam/air at high temperatures. To improve the effectiveness of operation, one can go in for the multistage counter operation with regeneration. In these operations one has to take care to minimize or prevent the carry over of solids.

12.12.3 Steady-state Moving Bed Adsorbers

In this category of adsorbers both the solids and fluid move continuously. The composition at any particular point is independent of time. They are operated with the solids moving downwards and the liquid in upward direction. The flow of solids is plug flow in nature and it is not in fluidized state.

The Higgins contactor developed for ion exchange is an excellent facility for adsorption. Figure 12.19 indicates the arrangement. This consists of two sections. In the top section to start with adsorption takes place. Simultaneously the bottom section of the bed undergoes regeneration. After some pre-calculated duration of operation, the flow of liquids is stopped and the positions of the valves are changed

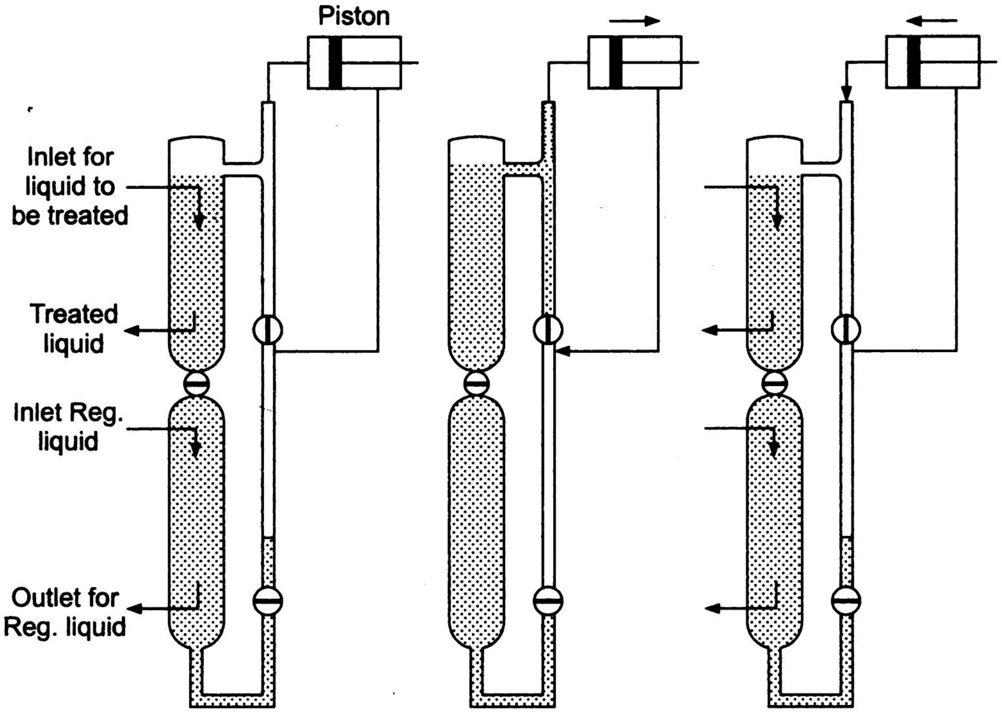


Fig. 12.19 Higgins contactor.

as indicated. The liquid-filled piston pump is moved and this leads to the clockwise movement of solids. Once again the valves are moved to their original position and the movement of solid also stops. The adsorption cycle once again starts in the top section of the unit and desorption at the bottom section.

WORKED EXAMPLES

1. One litre flask is containing air and acetone at 1 atm and 303 K with a relative humidity of 35% of acetone. 2 g of fresh activated carbon is introduced and the flask is scaled. Compute the final vapour composition and final pressure neglecting adsorption of air.

Equilibrium data:

g adsorbed/g carbon	0	0.1	0.2	0.3	0.35
Partial pressure of acetone, mm Hg	0	2	12	42	92

Vapour pressure of acetone at 30°C is 283 mm Hg.

Solution.

Let us convert the data from partial pressure to concentration in terms of g acetone/g of air.

i.e. $$\frac{2}{(760-2)} \times \frac{58}{28.84} = 5.28 \times 10^{-3} \text{ g acetone/g air}$$

Likewise the other values can also be converted to concentration in terms of mass ratios.

Hence,

X, g adsorbed/g carbon	0	0.1	0.2	0.3	0.35
Y, g acetone/g air	0	5.28×10^{-3}	32.1×10^{-3}	117×10^{-3}	276×10^{-3}

Originally the feed contains 35% RH acetone

i.e. Partial pressure/vapour pressure = 0.35

∴ Partial pressure of acetone = 283 × 0.35 = 99 mm Hg.

Partial pressure of air = 661 mm Hg.

$$\therefore \quad Y_0 = \frac{99}{(760-99)} \times \frac{58}{28.84} = 0.301 \text{ g of acetone/g of air}$$

$$L_S = 2 \text{ g}$$

The feed point is $(X_0, Y_0) = (0.0, 0.301)$

Volume fraction of air in the original mixture = $\frac{(760-99)}{760} = 0.87$ liters.

i.e. volume of air = 0.87 l (At 1 atm and 303 K)

i.e. moles of air = $\frac{(0.87 \times 1)}{303} \times \frac{273}{1} \times \frac{1}{22.414} = 0.03496$ g moles

i.e. mass of air in the original mixture = 0.03496 × 28.84 = 1.008 g

$$\therefore \quad \frac{L_S}{G_S} = \frac{2}{1.008} = 1.984$$

$$Y_1 \text{ (from graph)} = 13 \times 10^{-3} \text{ g acetone/g air}$$

Grams of acetone left behind after adsorption, per gram of air = 0.013

$$\text{i.e.} \quad \frac{\text{Partial pressure of acetone}}{\text{Partial pressure of air}} \times \frac{58}{28.84} = \text{g acetone/g air}$$

$$\text{i.e.} \quad \frac{\text{Partial pressure of acetone}}{661} \times \frac{58}{28.84} = 0.013 \text{ g acetone/g air}$$

∴ Partial pressure of acetone in flask after adsorption = 4.27 mm Hg

∴ Total pressure = 661 + 4.27 = 665.27 mm Hg.

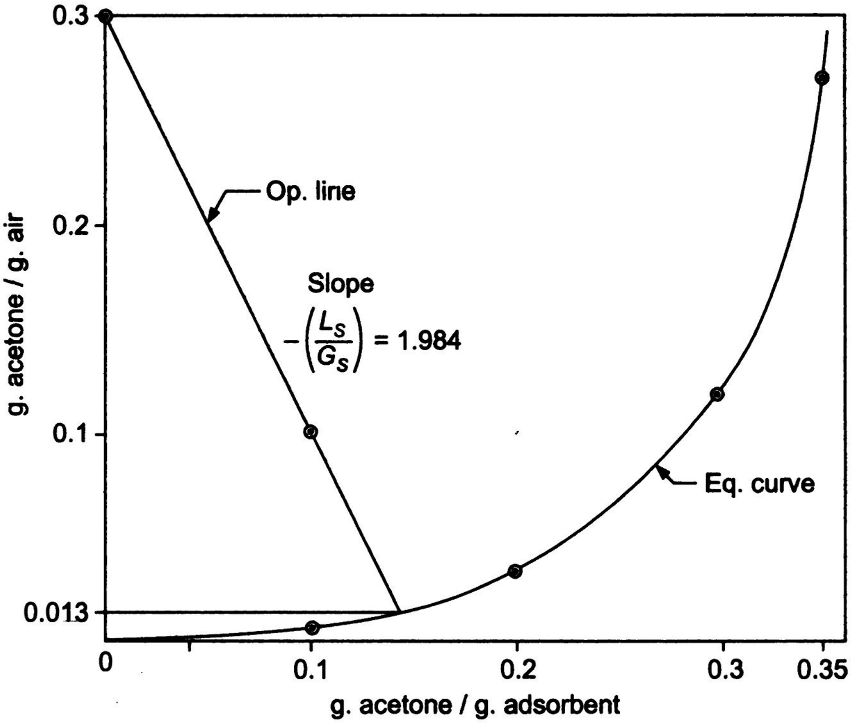


Fig. 12.20 Example 1.

2. A solid adsorbent is used to remove colour impurity from an aqueous solution. The original value of colour on an arbitrary scale is 48. It is required to reduce this to 10% of its original value. Using the following data, find the quantity of fresh adsorbent used for 1000 kg of solution for (a) a single stage and (b) a two-stage cross-current operation when the intermediate colour value is 24.

   Equilibrium data:

kg adsorbent/kg of solution	0	0.001	0.004	0.008	0.02	0.04
Equilibrium colour (Y)	48	43	31.5	21.5	8.5	3.5

Solution.

(a) The given data will be converted to enable us to handle it more easily.

The initial values are X_o = units of colour/kg adsorbent = 0

Y_o = units of colour/kg solution = 48

When 0.001 kg of adsorbent is added to1 kg of solution, the colour reduces from 48 units to 43 units. These 5 units of colour are thus transferred to 0.001 kg adsorbent.

$$\therefore \qquad X, \frac{\text{units of colour}}{\text{kg adsorbent}} = \frac{(48-43)}{0.001} = 5000$$

Similarly, by adding 0.004 kg adsorbent, colour drops by 16.5 units.

$$\text{i.e.} \qquad X = \frac{16.5}{0.004} = 4125$$

X, colour adsorbent/kg adsorbent	0	5000	4125	3312.5	1975	1112.5
Y, colour/kg solution	48	43	31.5	21.5	8.5	3.5

The final solution has 4.8 units of colour

(a) *Single stage operation:*

$$\text{Slope} = -\frac{L_S}{G_S} = -0.030 \text{ (from graph)}$$

G_S is 1000 kg of solution.

$\therefore$ Dosage of carbon = 0.03 × 1000 = 30 kg

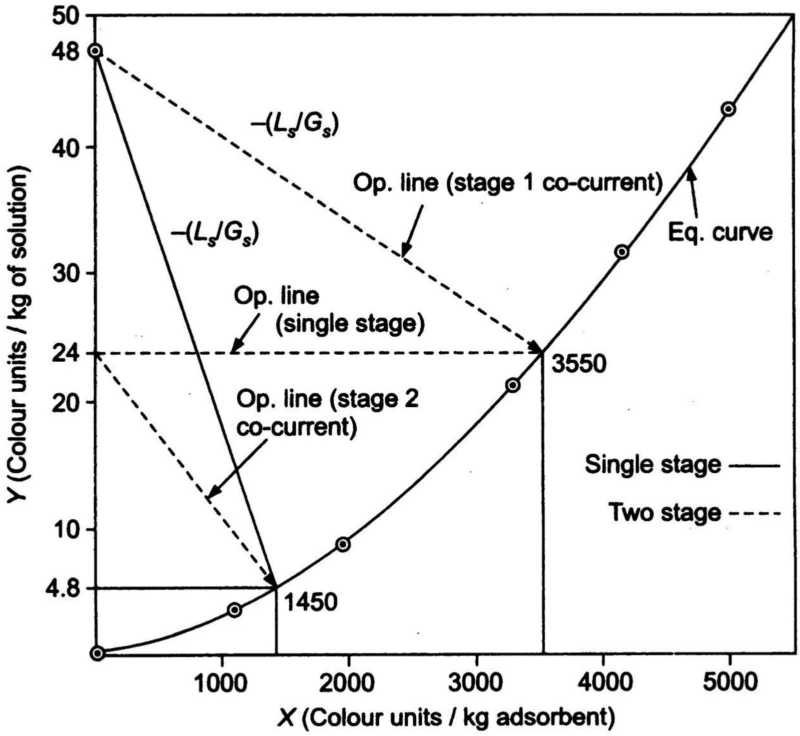


Fig. 12.21 Example 2.

(b) A two-stage cross-current operation

$$-\left(\frac{L_S}{G_S}\right)_1 = +\frac{(48-24)}{(0-3550)} = -\frac{24}{3550} = -6.76 \times 10^{-3}$$

$$-\left(\frac{L_S}{G_S}\right)_2 = +\frac{(24-4.8)}{(-1450+0)} = -0.01324$$

G_S is 1000 kg of solution

$\therefore$ $L_{S_1} + L_{S_2} = 6.76 + 13.24 = 20.00$ kg

3. The equilibrium decolourisation data for a certain system using activated carbon is given by the equation,

$$Y = 0.004X^2$$

where Y is g colouring impurity/kg impurity free solution and X is g colouring impurity/kg pure activated carbon.

Calculate the amount of activated carbon required per 1000 kg of impurity free solution to reduce the impurity concentration from 1.2 to 0.2 g/kg of impurity free solution using (i) a single stage operation and (ii) a two-stage cross-current operation with intermediate composition of 0.5 g. of colouring impurity per kg of impurity free solution.

$$Y = 0.004X^2$$

Solution.

Feed, G_S = 1000 kg of impurity free solution

(i) Y_0 = 1.2 g/kg of impurity free solution

Y_1 = 0.2 g/kg of impurity free solution

$X_0 = 0$

$$X_1 = \left(\frac{Y_1}{0.004}\right)^{0.5} = \left(\frac{0.2}{0.004}\right)^{0.5} = 7.07$$

$$-\frac{L_S}{G_S} = +\frac{(Y_0 - Y_1)}{(X_0 - X_1)} = +\frac{(1.2-0.2)}{(0-7.07)} = -\frac{1}{7.07} = -0.1414$$

$\therefore$ $L_S = 0.1414 \times 1000 = 141.4$ kg of adsorbent

(ii) Intermediate colour concentration is 0.5 g/kg of impurity free solution

$$\therefore \quad X_1 = \left(\frac{0.5}{0.004}\right)^{0.5} = 11.18$$

$$\therefore \quad -\left(\frac{L_S}{G_S}\right)_1 = \frac{(1.2-0.5)}{(0-11.18)} = -\frac{0.7}{11.18} = -0.06261$$

$$X_2 = X_{\text{final}} = 7.07$$

$$-\left(\frac{L_S}{G_S}\right)_2 = \frac{(0.5-0.2)}{(0-7.07)} = -0.04243$$

$$\therefore \qquad \left(\frac{L_S}{G_S}\right)_{\text{total}} = 0.06261 + 0.04243 = 0.10504$$

The adsorbent needed, L_S = 105.04 kg of adsorbent.

4. A solution of washed raw cane sugar of 48% sucrose by weight is coloured by the presence of small quantities of impurities. It is to be decolourised at 80°C by treatment with an adsorptive carbon in a contact filtration plant. The data for an equilibrium adsorption isotherm were obtained by adding various amounts of the carbon to separate batches of the original solution and observing the equilibrium colour reached in each case. The data with the quantity of carbon expressed on the basis of the sugar content of the solution are as follows:

$\frac{\text{kg carbon}}{\text{kg dry sugar}}$	0	0.005	0.01	0.015	0.02	0.03
% colour removed	0	47	70	83	90	95

The original solution has a colour concentration of 20 measured on an arbitrary scale and it is desired to reduce the colour to 2.5% of its original value.

(i) Convert the equilibrium data to Y and X.

(ii) Calculate the amount of carbon required for a single stage process for a feed of 1000 kg solution.

(iii) Estimate the amount of carbon needed for a feed of 1000 kg solution in a two-stage countercurrent process.

Solution.

Feed solution contains 48% sucrose.

$\frac{\text{kg carbon}}{\text{kg dry sugar}}$	0	0.005	0.01	0.015	0.02	0.03
% colour removed	0	47	70	83	90	95
$\frac{\text{kg carbon}}{\text{kg dry solution}}$	0	0.0024	0.0048	0.0072	0.0096	0.0144
$Y, \frac{\text{colour}}{\text{kg of solution}}$	20	0.53×20 $=10.6$	0.30×20 $=6$	0.17×20 $=3.4$	0.10×20 $=2.0$	0.05×20 $=1.0$
$X, \frac{\text{colour}}{\text{kg carbon}}$	–	$\frac{(20-10.6)}{0.0024}$ $=3916.7$	$\frac{(20-6)}{0.0048}$ $=2916.7$	$\frac{(20-3.4)}{0.0072}$ $=2305.6$	$\frac{(20-2)}{0.0096}$ $=1875$	$\frac{(20-1)}{0.0144}$ $=1319.4$

Feed is $(X_0, Y_0) = (0, 20)$

Final product is to have 2.5% original colour, i.e. 0.5 units = Y_1

$$\therefore \qquad -\left(\frac{L_S}{G_S}\right) = \frac{(20-0.5)}{(0-100)} = -\frac{19.5}{1000} = -0.0195$$

$$\therefore \qquad L_S = G_S \times 0.0195 = 19.5 \text{ kg}$$

(ii) The operating line is fixed by trial and error for exactly two stages.

$$\left(\frac{L_S}{G_S}\right) = \frac{19.5}{3175} = 6.142 \times 10^{-3}$$

$$\therefore \qquad L_S = 6.142 \text{ kg}$$

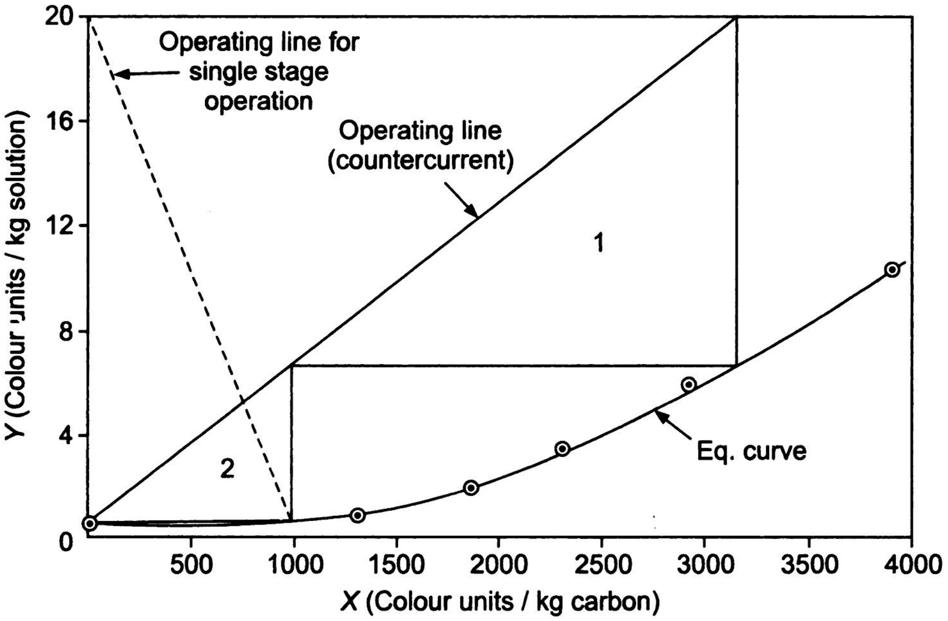


Fig. 12.22 Example 4.

5. NO$_2$ produced by a thermal process for fixation of nitrogen is to be removed from a dilute mixture with air by adsorption on silica gel in a continuous countercurrent adsorber. The gas entering at the rate of 0.126 kg/s contains 1.5% of NO$_2$ by volume and 90% of NO$_2$ is to be removed. Operation is isothermal at 25°C and 1 atm pressure. The entering gel will be free of NO$_2$.

Partial pressure of NO$_2$, mm Hg	0	2	4	6	8	10	12
kg NO$_2$/100 kg gel	0	0.4	0.9	1.65	2.6	3.65	4.85

(a) Calculate the minimum weight of gel required/h.

(b) For twice the minimum gel rate, calculate the number of stages required.

Solution.

Entering gas rate : 450 kg/hr = 0.126 kg/s

NO$_2$ present : 1.5 % by volume

Temperature : 25°C

Pressure : 1 std. atm.

Partial pressure of NO_2, mm Hg	0	2	4	6	8	10	12
kg NO_2/100 kg gel	0	0.4	0.9	1.65	2.6	3.65	4.85
Kg NO_2/kg gel, X	0	0.004	0.009	0.0165	0.026	0.0365	0.0485
(pp NO_2/pp air) × (46/28.84), Y, (kg/kg)	0	0.0042	0.00844	0.01269	0.01697	0.02127	0.0256

$$Y_{in} = 1.5\%$$

$$Y_{in} = (\text{kg/kg}) = \frac{1.5}{98.5} \times \frac{46}{28.84} = 0.0243$$

$$Y_{in}\ (\text{kg/kg of mixture})\ \frac{0.0243}{1.0243} = 0.0237$$

$$G_S = 450\ (1 - 0.0237) = 439.3\ \text{kg/h}$$

90% of NO_2 is to be recovered

$$Y_{out} = \frac{1.5 \times 0.1}{98.5} \times \frac{46}{28.84} = 0.00243$$

$$\left(\frac{L_S}{G_S}\right)_{min} = \frac{0.025}{0.0375} = 0.667$$

Weight of absorbent required, $L_S = 0.667 \times 439.3 = 291.1$ kg/h

Number of stages needed for twice the adsorbent rate

$$\therefore \qquad \left(\frac{L_S}{G_S}\right)_{act} = \frac{582.2}{439.3} = 1.334$$

No. of stages = 3

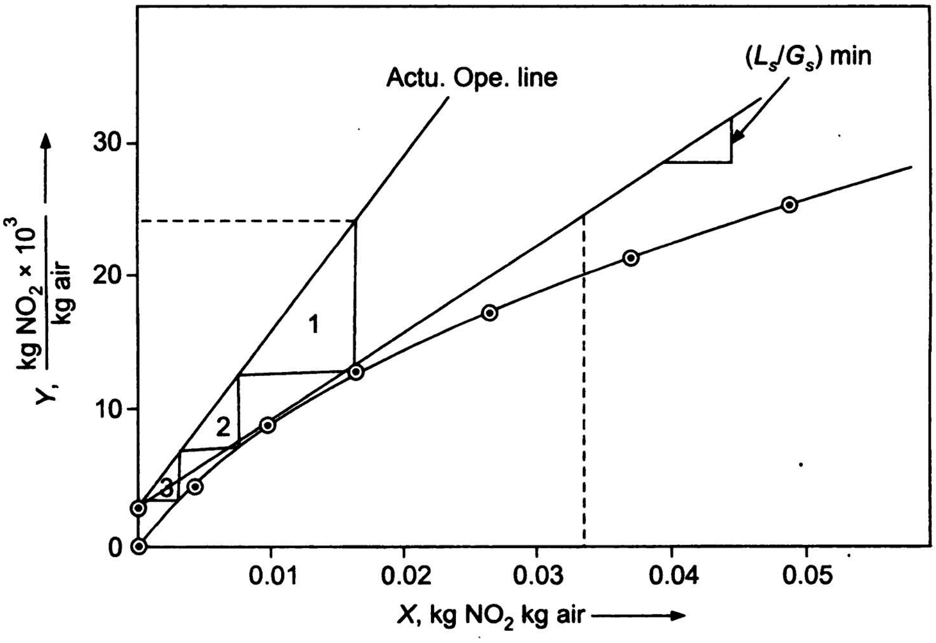


Fig. 12.23 Example 5.

6. 500 kg/min of dry air at 20°C and carrying 5 kg of water vapour/min. is to be dehumidified with silica gel to 0.001 kg of water vapour/kg of dry air. The operation has to be carried out isothermally and countercurrently with 25 kg/min. of dry silica gel. How many theoretical stages are required and what will be the water content in the silica gel leaving the last stage?

kg. of water vapour/ kg of dry silica gel, X	0	0.05	0.10	0.15	0.20
kg of water vapour/ kg of dry air, Y	0	0.0018	0.0036	0.0050	0.0062

Solution.

Quantity of dry air entering at 20°C, G_S = 500 kg/min

Quantity of water vapour entering = 5 kg/min

$$Y_1 = \frac{5}{500} = 0.01 \text{ kg water vapour/kg dry air}$$

Concentration of water vapour in leaving air, Y_2 = 0.001 kg water vapour/ kg dry air

Quantity of silica gel entering, L_S = 25 kg/min

$$X_2 = 0$$

i.e.

$$\left(\frac{L_S}{G_S}\right) = \frac{25}{500} = 0.05$$

Making a material balance

$$L_S\,[X_1 - X_2] = G_S\,[Y_1 - Y_2]$$

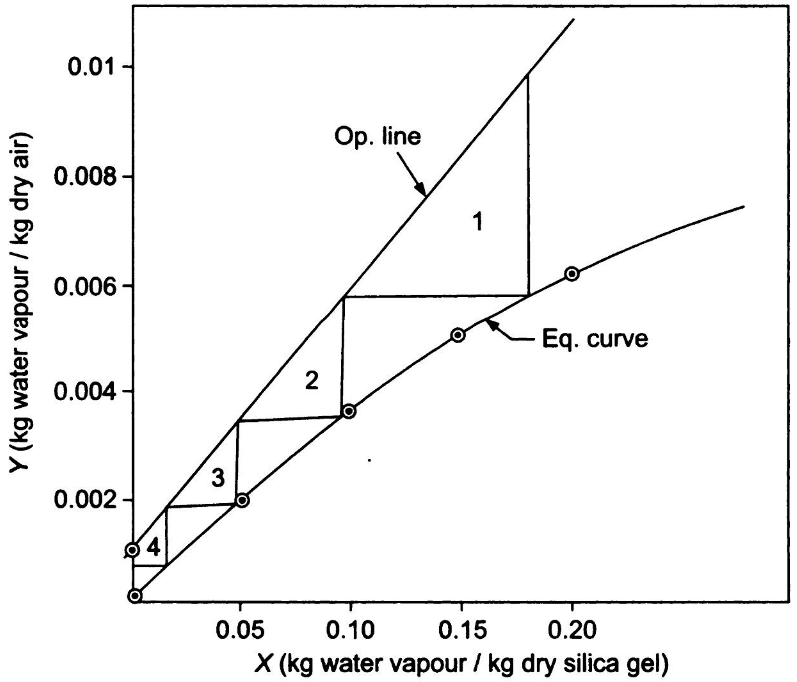


Fig. 12.24 Example 6.

$$\therefore \qquad X_1 = \frac{500 \times 0.009}{25} = 0.18$$

Total number of stages needed = 4