

Absorption of Gases

12.1. INTRODUCTION

The removal of one or more selected components from a mixture of gases by absorption into a suitable liquid is the second major operation of chemical engineering that is based on interphase mass transfer controlled largely by rates of diffusion. Thus, acetone can be recovered from an acetone–air mixture by passing the gas stream into water in which the acetone dissolves while the air passes out. Similarly, ammonia may be removed from an ammonia–air mixture by absorption in water. In each of these examples the process of absorption of the gas in the liquid may be treated as a physical process, the chemical reaction having no appreciable effect. When oxides of nitrogen are absorbed in water to give nitric acid, however, or when carbon dioxide is absorbed in a solution of sodium hydroxide, a chemical reaction occurs, the nature of which influences the actual rate of absorption. Absorption processes are therefore conveniently divided into two groups, those in which the process is solely physical and those where a chemical reaction is occurring. In considering the design of equipment to achieve gas absorption, the main requirement is that the gas should be brought into intimate contact with the liquid, and the effectiveness of the equipment will largely be determined by the success with which it promotes contact between the two phases. The general form of equipment is similar to that described for distillation in Chapter 11, and packed and plate towers are generally used for large installations. The method of operation, as will be seen later, is not the same. In absorption, the feed is a gas introduced at the bottom of the column, and the solvent is fed to the top, as a liquid; the absorbed gas and solvent leave at the bottom, and the unabsorbed components leave as gas from the top. The essential difference between distillation and absorption is that in the former the vapour has to be produced in each stage by partial vaporisation of the liquid which is therefore at its boiling point, whereas in absorption the liquid is well below its boiling point. In distillation there is a diffusion of molecules in both directions, so that for an ideal system equimolecular counterdiffusion takes place, though in absorption gas molecules are diffusing into the liquid, with negligible transfer in the reverse direction, as discussed in Volume 1, Chapter 10. In general, the ratio of the liquid to the gas flowrate is considerably greater in absorption than in distillation with the result that layout of the trays is different in the two cases. Furthermore, with the higher liquid rates in absorption, packed columns are much more commonly used.

12.2. CONDITIONS OF EQUILIBRIUM BETWEEN LIQUID AND GAS

When two phases are brought into contact they eventually reach equilibrium. Thus, water in contact with air evaporates until the air is saturated with water vapour, and the air is absorbed by the water until it becomes saturated with the individual gases. In any mixture of gases, the degree to which each gas is absorbed is determined by its partial pressure. At a given temperature and concentration, each dissolved gas exerts a definite partial pressure. Three types of gases may be considered from this aspect—a very soluble one, such as ammonia, a moderately soluble one, such as sulphur dioxide, and a slightly soluble one, such as oxygen. The values in Table 12.1 show the concentrations in kilograms per 1000 kg of water that are required to develop a partial pressure of 1.3, 6.7, 13.3, 26.7, and 66.7 kN/m² at 303 K. It may be seen that a slightly soluble gas requires a much higher partial pressure of the gas in contact with the liquid to give a solution of a given concentration. Conversely, with a very soluble gas a given concentration in the liquid phase is obtained with a lower partial pressure in the vapour phase. At 293 K a solution of 4 kg of sulphur dioxide per 1000 kg of water exerts a partial pressure of 2.7 kN/m². If a gas is in contact with this solution with a partial pressure SO₂ greater than 2.7 kN/m², sulphur dioxide will be absorbed. The most concentrated solution that can be obtained is that in which the partial pressure of the solute gas is equal to its partial pressure in the gas phase. These equilibrium conditions fix the limits of operation of an absorption unit. Thus, in an ammonia–air mixture containing 13.1 per cent of ammonia, the partial pressure of the ammonia is 13.3 kN/m² and the maximum concentration of the ammonia in the water at 303 K is 93 kg per 1000 kg of water.

Table 12.1. Partial pressures and concentrations of aqueous solutions of gases at 303 K

Partial pressure of solute in gas phase (kN/m ²)	Concentration of solute in water kg/1000 kg water		
	Ammonia	Sulphur dioxide	Oxygen
1.3	11	1.9	—
6.7	50	6.8	—
13.3	93	12	0.008
26.7	160	24.4	0.013
66.7	315	56	0.033

Whilst the solubility of a gas is not substantially affected by the total pressure in the system for pressures up to about 500 kN/m², it is important to note that the solubility falls with a rise of temperature. Thus, for a concentration of 25 per cent by mass of ammonia in water, the equilibrium partial pressure of the ammonia is 30.3 kN/m² at 293 K and 46.9 kN/m² at 303 K.

In many instances the absorption is accompanied by the evolution of heat, and it is therefore necessary to fit coolers to the equipment to keep the temperature sufficiently low for an adequate degree of absorption to be obtained.

For dilute concentrations of most gases, and over a wide range for some gases, the equilibrium relationship is given by Henry's law. This law, as used in Chapter 11, can be written as:

$$P_A = \mathcal{H}C_A \quad (12.1)$$

where: P_A is the partial pressure of the component A in the gas phase,
 C_A is the concentration of the component in the liquid, and
 \mathcal{H} is Henry's constant.

12.3. THE MECHANISM OF ABSORPTION

12.3.1. The two-film theory

The most useful concept of the process of absorption is given by the two-film theory due to WHITMAN⁽¹⁾, and this is explained fully in Volume 1, Chapter 10. According to this theory, material is transferred in the bulk of the phases by convection currents, and concentration differences are regarded as negligible except in the vicinity of the interface between the phases. On either side of this interface it is supposed that the currents die out and that there exists a thin film of fluid through which the transfer is effected solely by molecular diffusion. This film will be slightly thicker than the laminar sub-layer, because it offers a resistance equivalent to that of the whole boundary layer. According to Fick's law (Volume 1, equation 10.1) the rate of transfer by diffusion is proportional to the concentration gradient and to the area of interface over which the diffusion is occurring. Fick's law is limited to cases where the concentration of the absorbed component is low. At high concentrations, bulk flow occurs and the mass transfer rate, which is increased by a factor C_T/C_B , is governed by Stefan's law, equation 12.2. Under these circumstances, the concentration gradient is no longer constant throughout the film and the lines AB and DE are curved. This question has been discussed in Chapter 10 of Volume 1, but some of the important features will be given here.

The direction of transfer of material across the interface is not dependent solely on the concentration difference, but also on the equilibrium relationship. Thus, for a mixture of ammonia or hydrogen chloride and air which is in equilibrium with an aqueous solution, the concentration in the water is many times greater than that in the air. There is, therefore, a very large concentration gradient across the interface, although this is not the controlling factor in the mass transfer, as it is generally assumed that there is no resistance at the interface itself, where equilibrium conditions will exist. The controlling factor will be the rate of diffusion through the two films where all the resistance is considered to lie. The change in concentration of a component through the gas and liquid phases is illustrated in Figure 12.1. P_{AG} represents the partial pressure in the bulk of the gas phase and P_{Ai} the partial pressure at the interface. C_{AL} is the concentration in the bulk of the liquid phase and C_{Ai} the concentration at the interface. Thus, according to this theory, the concentrations at the interface are in equilibrium, and the resistance to transfer is centred in the thin films on either side. This type of problem is encountered in heat transfer across a tube, where the main resistance to transfer is shown to lie in the thin films on either side of the wall; here the transfer is by conduction.

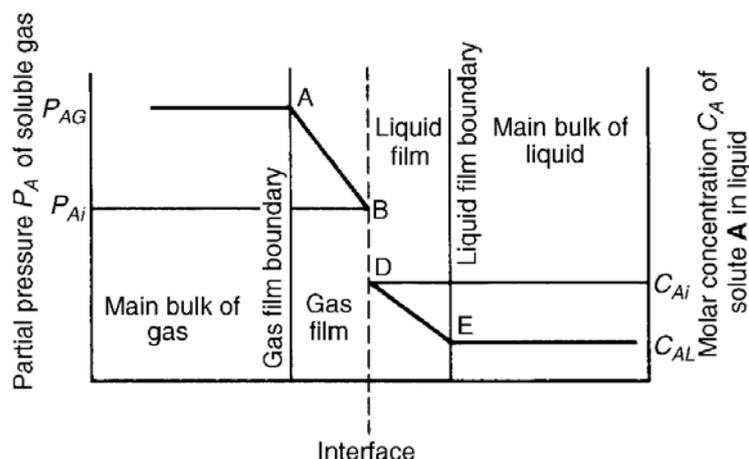


Figure 12.1. Concentration profile for absorbed component A

12.3.2. Application of mass transfer theories

The preceding analysis of the process of absorption is based on the two-film theory of WHITMAN⁽¹⁾. It is supposed that the two films have negligible capacity, but offer all the resistance to mass transfer. Any turbulence disappears at the interface or free surface, and the flow is thus considered to be laminar and parallel to the surface.

An alternative theory described in detail in Volume 1, Chapter 10, has been put forward by HIGBIE⁽²⁾, and later extended by DANCKWERTS⁽³⁾ and DANCKWERTS and KENNEDY⁽⁴⁾ in which the liquid surface is considered to be composed of a large number of small elements each of which is exposed to the gas phase for an interval of time, after which they are replaced by fresh elements arising from the bulk of the liquid.

All three of these proposals give the mass transfer rate N'_A directly proportional to the concentration difference ($C_{Ai} - C_{AL}$) so that they do not directly enable a decision to be made between the theories. However, in the Higbie–Danckwerts theory $N'_A \propto \sqrt{D_L}$ whereas $N'_A \propto D_L$ in the two-film theory. DANCKWERTS⁽³⁾ applied this theory to the problem of absorption coupled with chemical reaction but, although in this case the three proposals give somewhat different results, it has not been possible to distinguish between them.

The application of the penetration theory to the interpretation of experimental results obtained in wetted-wall columns has been studied by LYNN, STRAATEMEIER, and KRAMERS⁽⁵⁾. They absorbed pure sulphur dioxide in water and various aqueous solutions of salts and found that, in the presence of a trace of Teepol which suppressed ripple formation, the rate of absorption was closely predicted by the theory. In very short columns, however, the rate was overestimated because of the formation of a region in which the surface was stagnant over the bottom one centimetre length of column. The studies were extended to columns containing spheres and again the penetration theory was found to hold, there being very little mixing of the surface layers with the bulk of the fluid as it flowed from one layer of spheres to the next.

Absorption experiments in columns packed with spheres, 37.8 mm diameter, were also carried out by DAVIDSON *et al.*⁽⁶⁾ who absorbed pure carbon dioxide into water. When a small amount of surface active agent was present in the water no appreciable mixing was

found between the layers of spheres. With pure water, however, the liquid was almost completely mixed in this region.

DAVIDSON⁽⁷⁾ built up theoretical models of the surfaces existing in a packed bed, and assumed that the liquid ran down each surface in laminar flow and was then fully mixed before it commenced to run down the next surface. The angles of inclination of the surfaces were taken as random. In the first theory it was assumed that all the surfaces were of equal length, and in the second that there was a random distribution of surface lengths up to a maximum. Thus the assumptions regarding age distribution of the liquid surfaces were similar to those of HIGBIE⁽²⁾ and DANCKWERTS⁽³⁾. Experimental results were in good agreement with the second theory. All random packings of a given size appeared to be equivalent to a series of sloping surfaces, and therefore the most effective packing would be that which gave the largest interfacial area.

In an attempt to test the surface renewal theory of gas absorption, DANCKWERTS and KENNEDY⁽⁸⁾ measured the transient rate of absorption of carbon dioxide into various solutions by means of a rotating drum which carried a film of liquid through the gas. Results so obtained were compared with those for absorption in a packed column and it was shown that exposure times of at least one second were required to give a strict comparison; this was longer than could be obtained with the rotating drum. ROBERTS and DANCKWERTS⁽⁹⁾ therefore used a wetted-wall column to extend the times of contact up to 1.3 s. The column was carefully designed to eliminate entry and exit effects and the formation of ripples. The experimental results and conclusions are reported by DANCKWERTS, KENNEDY, and ROBERTS⁽¹⁰⁾ who showed that they could be used, on the basis of the penetration theory model, to predict the performance of a packed column to within about 10 per cent.

There have been many recent studies of the mechanism of mass transfer in a gas absorption system. Many of these have been directed towards investigating whether there is a significant resistance to mass transfer at the interface itself. In order to obtain results which can readily be interpreted, it is essential to operate with a system of simple geometry. For that reason a laminar jet has been used by a number of workers.

CULLEN and DAVIDSON⁽¹¹⁾ studied the absorption of carbon dioxide into a laminar jet of water. When the water issued with a uniform velocity over the cross-section, the measured rate of absorption corresponded closely with the theoretical value. When the velocity profile in the water was parabolic, the measured rate was lower than the calculated value; this was attributed to a hydrodynamic entry effect.

The possible existence of an interface resistance in mass transfer has been examined by RAIMONDI and TOOR⁽¹²⁾ who absorbed carbon dioxide into a laminar jet of water with a flat velocity profile, using contact times down to 1 ms. They found that the rate of absorption was not more than 4 per cent less than that predicted on the assumption of instantaneous saturation of the surface layers of liquid. Thus, the effects of interfacial resistance could not have been significant. When the jet was formed at the outlet of a long capillary tube so that a parabolic velocity profile was established, absorption rates were lower than predicted because of the reduced surface velocity. The presence of surface-active agents appeared to cause an interfacial resistance, although this effect is probably attributable to a modification of the hydrodynamic pattern.

STERNLING and SCRIVEN⁽¹³⁾ have examined interfacial phenomena in gas absorption and have explained the interfacial turbulence which has been noted by a number of workers in

terms of the Marangoni effect which gives rise to movement at the interface due to local variations in interfacial tension. Some systems have been shown to give rise to stable interfaces when the solute is transferred in one direction, although instabilities develop during transfer in the reverse direction.

GOODRIDGE and ROBB⁽¹⁴⁾ used a laminar jet to study the rate of absorption of carbon dioxide into sodium carbonate solutions containing a number of additives including glycerol, sucrose, glucose, and arsenites. For the short times of exposure used, absorption rates into sodium carbonate solution or aqueous glycerol corresponded to those predicted on the basis of pure physical absorption. In the presence of the additives, however, the process was accelerated as the result of chemical reaction.

Absorption of gases and vapour by drops has been studied by GARNER and KENDRICK⁽¹⁵⁾ and GARNER and LANE⁽¹⁶⁾ who developed a vertical wind tunnel in which drops could be suspended for considerable periods of time in the rising gas stream. During the formation of each drop the rate of mass transfer was very high because of the high initial turbulence. After the initial turbulence had subsided, the mass transfer rate approached the rate for molecular diffusion provided that the circulation had stopped completely. In a drop with stable natural circulation the rate was found to approach 2.5 times the rate for molecular diffusion.

12.3.3. Diffusion through a stagnant gas

The process of absorption may be regarded as the diffusion of a soluble gas **A** into a liquid. The molecules of **A** have to diffuse through a stagnant gas film and then through a stagnant liquid film before entering the main bulk of liquid. The absorption of a gas consisting of a soluble component **A** and an insoluble component **B** is a problem of mass transfer through a stationary gas to which Stefan's law (Volume 1, Chapter 10) applies:

$$N'_A = -D_V \frac{C_T}{C_B} \frac{dC_A}{dz} \quad (12.2)$$

where N'_A is the overall rate of mass transfer (moles/unit area and unit time),
 D_V is the gas-phase diffusivity,
 z is distance in the direction of mass transfer, and
 C_A , C_B , and C_T are the molar concentrations of **A**, **B**, and total gas, respectively.

Integrating over the whole thickness z_G of the film, and representing concentrations at each side of the interface by suffixes 1 and 2:

$$N'_A = \frac{D_V C_T}{z_G} \ln \frac{C_{B2}}{C_{B1}} \quad (12.3)$$

Since $C_T = P/RT$, where **R** is the gas constant, T the absolute temperature, and P the total pressure. For an ideal gas, then:

$$N'_A = \frac{D_V P}{RT z_G} \ln \frac{P_{B2}}{P_{B1}} \quad (12.4)$$

Writing P_{Bm} as the log mean of the partial pressures P_{B1} and P_{B2} , then:

$$P_{Bm} = \frac{P_{B2} - P_{B1}}{\ln(P_{B2}/P_{B1})} \quad (12.5)$$

$$\begin{aligned} N'_A &= \frac{D_V P}{RT z_G} \frac{P_{B2} - P_{B1}}{P_{Bm}} \\ &= \frac{D_V P}{RT z_G} \left[\frac{P_{A1} - P_{A2}}{P_{Bm}} \right] \end{aligned} \quad (12.6)$$

Hence the rate of absorption of **A** per unit time per unit area is given by:

$$N'_A = k'_G P \left[\frac{P_{A1} - P_{A2}}{P_{Bm}} \right] \quad (12.7)$$

or:
$$N'_A = k_G (P_{A1} - P_{A2}) \quad (12.8)$$

where:
$$k'_G = \frac{D_V}{RT z_G}, \quad \text{and} \quad k_G = \frac{D_V P}{RT z_G P_{Bm}} = \frac{k'_G P}{P_{Bm}} \quad (12.9)$$

In the great majority of industrial processes the film thickness is not known, so that the rate equation of immediate use is equation 12.8 using k_G . k_G is known as the gas-film transfer coefficient for absorption and is a direct measure of the rate of absorption per unit area of interface with a driving force of unit partial pressure difference.

12.3.4. Diffusion in the liquid phase

The rate of diffusion in liquids is much slower than in gases, and mixtures of liquids may take a long time to reach equilibrium unless agitated. This is partly due to the much closer spacing of the molecules, as a result of which the molecular attractions are more important.

Whilst there is at present no theoretical basis for the rate of diffusion in liquids comparable with the kinetic theory for gases, the basic equation is taken as similar to that for gases, or for dilute concentrations:

$$N'_A = -D_L \frac{dC_A}{dz} \quad (12.10)$$

On integration:
$$N'_A = -D_L \left[\frac{C_{A2} - C_{A1}}{z_L} \right] \quad (12.11)$$

where: C_A, C_B are the molar concentrations of **A** and **B**,
 z_L is the thickness of liquid film through which diffusion occurs, and
 D_L is the diffusivity in the liquid phase.

Since the film thickness is rarely known, equation 12.11 is usually rewritten as:

$$N'_A = k_L (C_{A1} - C_{A2}) \quad (12.12)$$

which is similar to equation 12.8 for gases.

In equation 12.12, k_L is the liquid-film transfer coefficient, which is usually expressed in $\text{kmol/s m}^2(\text{kmol/m}^3) = \text{m/s}$. For dilute concentrations:

$$k_L = \frac{D_L}{z_L}$$

12.3.5. Rate of absorption

In a steady-state process of absorption, the rate of transfer of material through the gas film will be the same as that through the liquid film, and the general equation for mass transfer of a component **A** may be written as:

$$N'_A = k_G(P_{AG} - P_{Ai}) = k_L(C_{Ai} - C_{AL}) \tag{12.13}$$

where P_{AG} is the partial pressure in the bulk of the gas, C_{AL} is the concentration in the bulk of the liquid, and P_{Ai} and C_{Ai} are the values of concentration at the interface where equilibrium conditions are assumed to exist. Therefore:

$$\frac{k_G}{k_L} = \frac{C_{Ai} - C_{AL}}{P_{AG} - P_{Ai}} \tag{12.14}$$

These conditions may be illustrated graphically as in Figure 12.2, where ABF is the equilibrium curve for the soluble component **A**.

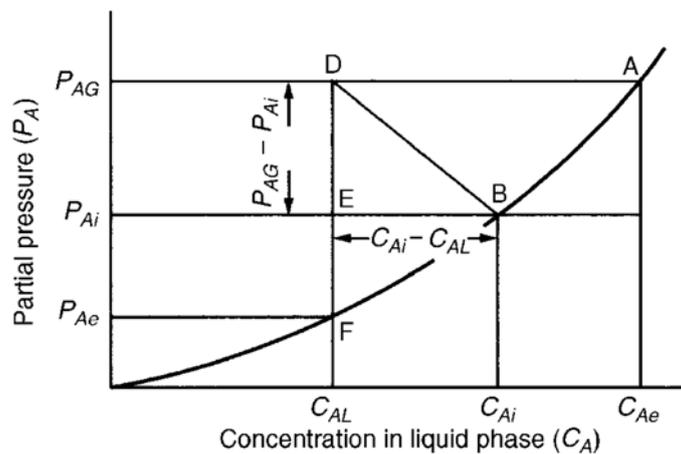


Figure 12.2. Driving forces in the gas and liquid phases

- Point D (C_{AL}, P_{AG}) represents conditions in the bulk of the gas and liquid.
 - P_{AG}) is the partial pressure of **A** in the main bulk of the gas stream, and
 - C_{AL}) is the average concentration of **A** in the main bulk of the liquid stream.
- Point A (C_{Ae}, P_{AG}) represents a concentration of C_{Ae} in the liquid in equilibrium with P_{AG} in the gas.

Point B (C_{Ai} , P_{Ai}) represents the concentration of C_{Ai} in the liquid in equilibrium with P_{Ai} in the gas, and gives conditions at the interface.

Point F (C_{AL} , P_{Ae}) represents a partial pressure P_{Ae} in the gas phase in equilibrium with C_{AL} in the liquid.

Then, the driving force causing transfer in the gas phase is:

$$(P_{AG} - P_{Ai}) \equiv DE$$

and the driving force causing transfer in the liquid phase is:

$$(C_{Ai} - C_{AL}) \equiv BE$$

Then:

$$\frac{P_{AG} - P_{Ai}}{C_{Ai} - C_{AL}} = \frac{k_L}{k_G}$$

and the concentrations at the interface (point B) are found by drawing a line through D of slope $-k_L/k_G$ to cut the equilibrium curve in B.

Overall coefficients

In order to obtain a direct measurement of the values of k_L and k_G the measurement of the concentration at the interface would be necessary. These values can only be obtained in very special circumstances, and it has been found of considerable value to use two overall coefficients K_G and K_L defined by:

$$N'_A = K_G(P_{AG} - P_{Ae}) = K_L(C_{Ae} - C_{AL}) \quad (12.15)$$

K_G and K_L are known as the overall gas and liquid phase coefficients, respectively.

Relation between film and overall coefficients

The rate of transfer of **A** may now be written as:

$$N'_A = k_G[P_{AG} - P_{Ai}] = k_L[C_{Ai} - C_{AL}] = K_G[P_{AG} - P_{Ae}] = K_L[C_{Ae} - C_{AL}]$$

Thus:

$$\begin{aligned} \frac{1}{K_G} &= \frac{1}{k_G} \left[\frac{P_{AG} - P_{Ae}}{P_{AG} - P_{Ai}} \right] \\ &= \frac{1}{k_G} \left[\frac{P_{AG} - P_{Ai}}{P_{AG} - P_{Ai}} \right] + \frac{1}{k_G} \left[\frac{P_{Ai} - P_{Ae}}{P_{AG} - P_{Ai}} \right] \end{aligned} \quad (12.16)$$

From the previous discussion:

$$\frac{1}{k_G} = \frac{1}{k_L} \left[\frac{P_{AG} - P_{Ai}}{C_{Ai} - C_{AL}} \right]$$

Thus:
$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k_L} \left[\frac{P_{AG} - P_{Ai}}{C_{Ai} - C_{AL}} \right] \left[\frac{P_{Ai} - P_{Ae}}{P_{AG} - P_{Ai}} \right]$$

$$= \frac{1}{k_G} + \frac{1}{k_L} \left[\frac{P_{Ai} - P_{Ae}}{C_{Ai} - C_{AL}} \right]$$

$(P_{Ai} - P_{Ae})/(C_{Ai} - C_{AL})$ is the average slope of the equilibrium curve and, when the solution obeys Henry's law, $\mathcal{H} = dP_A/dC_A \approx (P_{Ai} - P_{Ae})/(C_{Ai} - C_{AL})$.

Therefore:
$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{\mathcal{H}}{k_L} \tag{12.17}$$

Similarly:
$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{\mathcal{H}k_G} \tag{12.18}$$

and:
$$\frac{1}{K_G} = \frac{\mathcal{H}}{K_L} \tag{12.19}$$

A more detailed discussion of the relationship between film and overall coefficients is given in Volume 1, Chapter 10.

The validity of using equations 12.17 and 12.18 in order to obtain an overall transfer coefficient has been examined in detail by KING⁽¹⁷⁾. He has pointed out that the equilibrium constant \mathcal{H} must be constant, there must be no significant interfacial resistance, and there must be no interdependence of the values of the two film-coefficients.

Rates of absorption in terms of mole fractions

The mass transfer equations can be written as:

$$N'_A = k''_G(y_A - y_{Ai}) = K''_G(y_A - y_{Ae}) \tag{12.20}$$

and:
$$N'_A = k''_L(x_{Ai} - x_A) = K''_L(x_{Ae} - x_A) \tag{12.21}$$

where x_A, y_A are the mole fractions of the soluble component **A** in the liquid and gas phases, respectively.

$k''_G, k''_L, K''_G, K''_L$ are transfer coefficients defined in terms of mole fractions by equations 12.20 and 12.21.

If m is the slope of the equilibrium curve [approximately $(y_{Ai} - y_{Ae})/(x_{Ai} - x_A)$], it can then be shown that:

$$\frac{1}{K''_G} = \frac{1}{k''_G} + \frac{m}{k''_L} \tag{12.22}$$

which is similar to equation 11.151 used for distillation.

Factors influencing the transfer coefficient

The influence of the solubility of the gas on the shape of the equilibrium curve, and the effect on the film and overall coefficients, may be seen by considering three cases in turn — very soluble, almost insoluble, and moderately soluble gases.

(a) *Very soluble gas*. Here the equilibrium curve lies close to the concentration-axis and the points E and F are very close to one another as shown in Figure 12.2. The driving force over the gas film (DE) is then approximately equal to the overall driving force (DF), so that k_G is approximately equal to K_G .

(b) *Almost insoluble gas*. Here the equilibrium curve rises very steeply so that the driving force $(C_{Ai} - C_{AL})$ (EB) in the liquid film becomes approximately equal to the overall driving force $(C_{Ae} - C_{AL})$ (AD). In this case k_L will be approximately equal to K_L .

(c) *Moderately soluble gas*. Here both films offer an appreciable resistance, and the point B at the interface must be located by drawing a line through D of slope $-(k_L/k_G) = -(P_{AG} - P_{Ai})/(C_{Ai} - C_{AL})$.

In most experimental work, the concentration at the interface cannot be measured directly, and only the overall coefficients are therefore found. To obtain values for the film coefficients, the relations between k_G , k_L and K_G are utilised as discussed previously.

12.4. DETERMINATION OF TRANSFER COEFFICIENTS

In the design of an absorption tower, the most important single factor is the value of the transfer coefficient or the height of the transfer unit. Whilst the total flowrates of the gas and liquid streams are fixed by the process, it is necessary to determine the most suitable flow per unit area through the column. The gas flow is limited by the fact that the flooding rate must not be exceeded and there will be a serious drop in performance if the liquid rate is very low. It is convenient to examine the effects of flowrates of the gas and liquid on the transfer coefficients, and also to investigate the influence of variables such as temperature, pressure, and diffusivity.

In the laboratory, wetted-wall columns have been used by a number of workers and they have proved valuable in determining the importance of the various factors, and have served as a basis from which correlations have been developed for packed towers.

12.4.1. Wetted-wall columns

In many early studies, the rate of vaporisation of liquids into an air stream was measured in a wetted-wall column, similar to that shown in Figure 12.3. Logarithmic plots of d/z_G and $Re = du\rho/\mu$ gave a series of approximately straight lines and d/z_G was proportional to $Re^{0.83}$

where: d is the diameter of tube,

z_G is the thickness of gas film,

u is the gas velocity,

ρ is the gas density,

μ is the gas viscosity, and

B is a constant.

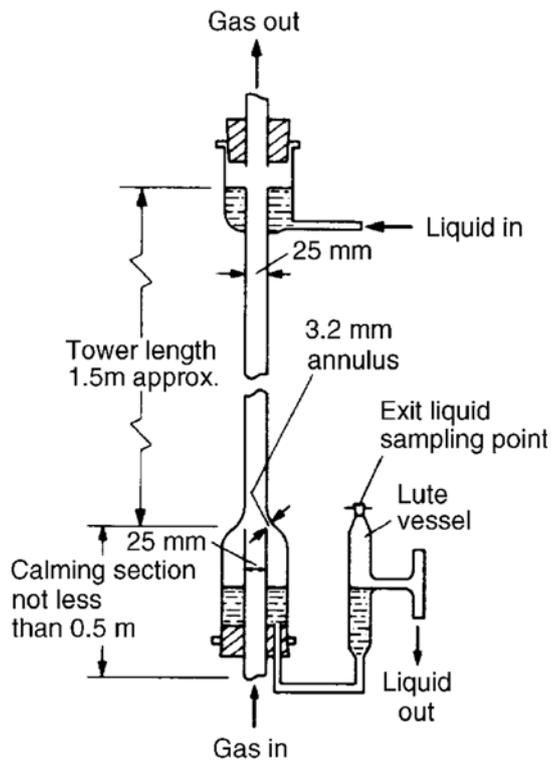


Figure 12.3. Diagram of a typical laboratory wetted-wall column

The unknown film thickness z_G may be eliminated as follows:

$$k_G = \frac{D_V P}{RT z_G P_{Bm}} \quad \text{(equation 12.9)}$$

Thus:
$$\frac{k_G RT P_{Bm}}{D_V P} = \frac{1}{z_G} = \frac{B}{d} Re^{0.83}$$

or:
$$\frac{h_D d P_{Bm}}{D_V P} = B Re^{0.83} \quad \text{(12.23)}$$

where $h_D = k_G RT$ is the mass transfer coefficient with the driving force expressed as a molar concentration difference.

GILLILAND and SHERWOOD'S data⁽¹⁸⁾, expressed by equation 12.23, are shown in Figure 12.4 for a number of systems. To allow for the variation in the physical properties, the Schmidt Group Sc is introduced, and the general equation for mass transfer in a wetted-wall column is then given by:

$$\frac{h_D d P_{Bm}}{D_V P} = B' Re^{0.83} Sc^{0.44} \quad \text{(12.24)}$$

Values of B' 0.021–0.027 have been reported and a mean value of 0.023 may be taken, which means that equation 12.24 very similar to the general heat transfer equation for forced convection in tubes (Volume 1, Chapter 9). The data shown in Figure 12.4 are

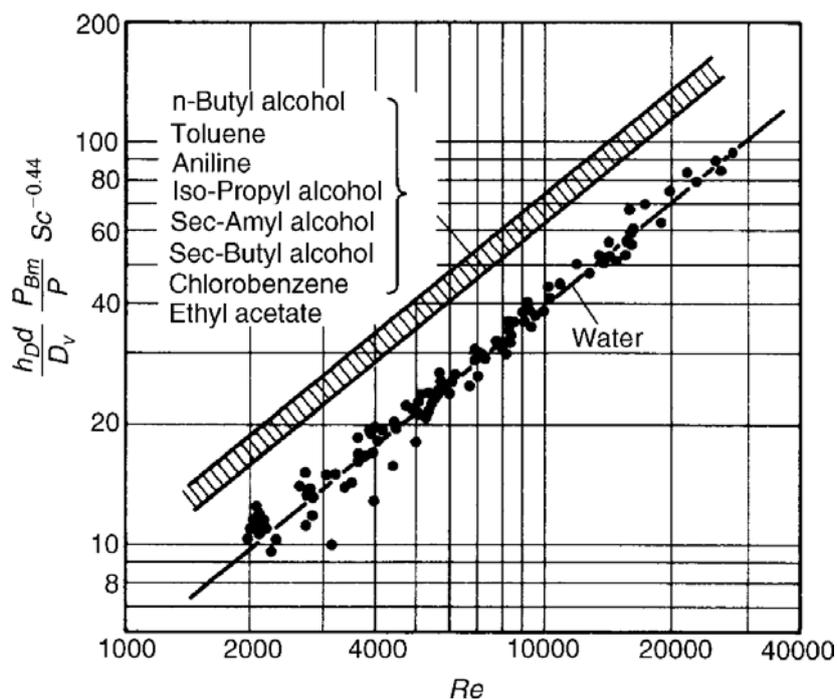


Figure 12.4. Vaporisation of liquids in a wetted-wall column

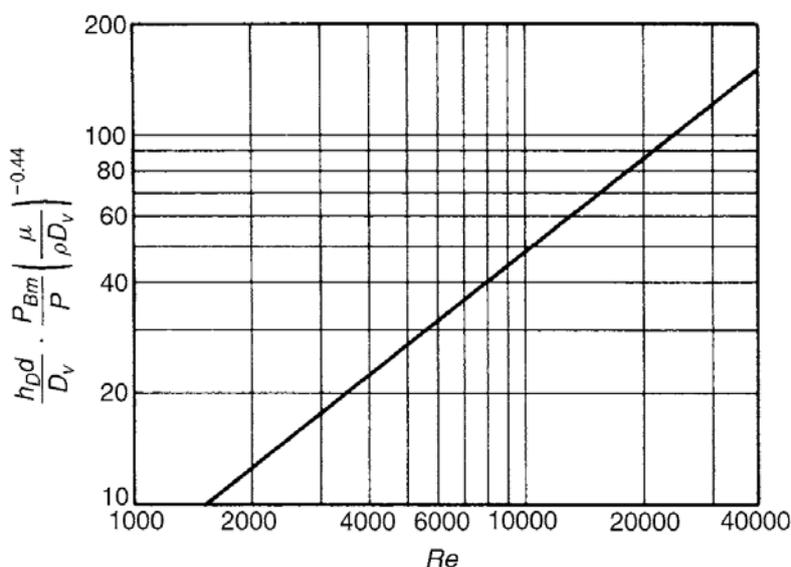


Figure 12.5. Correlation of data on the vaporisation of liquids in wetted-wall columns

replotted as $(h_{Dd}/D_V)(P_{Bm}/P)Sc^{-0.44}$ in Figure 12.5 and, in this way, they may be correlated by means of a single line.

In comparing the results of various workers, it is important to ensure that the inlet arrangements for the air are similar. Modifications of the inlet give rise to various values for the index on the Reynolds number, as found by HOLLINGS and SILVER⁽¹⁹⁾. A good calming length is necessary before the inlet to the measuring section, if the results are to be reproducible.

Equation 12.24 is frequently rearranged as:

$$\frac{h_D d}{D_V} \frac{P_{Bm}}{P} \frac{\mu}{du \rho} \left[\frac{\mu}{\rho D_V} \right]^{0.56} = B' Re^{-0.17} \left(\frac{\mu}{\rho D_V} \right)$$

or:

$$\frac{h_D}{u} \frac{P_{Bm}}{P} \left[\frac{\mu}{\rho D_V} \right]^{0.56} = B' Re^{-0.17} = j_d \quad (12.25)$$

where j_d is the j -factor for mass transfer as introduced by CHILTON and COLBURN⁽²⁰⁾ and discussed in Volume 1, Chapter 10. The main feature of this type of work is that $h_D \propto G^{0.8}$, $D_V^{0.56}$ and P/P_{Bm} . This form of relation is the basis for correlating data on packed towers.

Example 12.1

The overall liquid transfer coefficient, $K_L a$, for the absorption of SO₂ in water in a column is 0.003 kmol/s m³ (kmol/m³). By assuming an expression for the absorption of NH₃ in water at the same liquor rate and varying gas rates, derive an expression for the overall liquid film coefficient $K_L a$ for absorption of NH₃ in water in this equipment at the same water rate though with varying gas rates. The diffusivities of SO₂ and NH₃ in air at 273 K are 0.103 and 0.170 cm²/s. SO₂ dissolves in water, and Henry's constant is equal to 50 (kN/m²)/(kmol/m³). All data are expressed for the same temperature.

Solution

From equation 12.18:

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{\mathcal{H} k_G a} = \frac{1}{0.003} = 333.3$$

For the absorption of a moderately soluble gas it is reasonable to assume that the liquid and gas phase resistances are of the same order of magnitude, assuming them to be equal.

$$\frac{1}{k_L a} = \frac{1}{\mathcal{H} k_G a} = \left(\frac{333}{2} \right) = 166.7$$

or:

$$k_L a = \mathcal{H} k_G a = 0.006 \text{ kmol/s m}^3 \text{ (kmol/m}^3\text{)}$$

Thus, for SO₂: $k_G a = 0.006/\mathcal{H} = 0.006/50 = 0.00012 \text{ kmol/s m}^3 \text{ (kN/m}^2\text{)}$

From equation 12.25: $k_G a$ is proportional to (diffusivity)^{0.56}.

Hence for NH₃ : $k_G a = 0.00012(0.17/0.103)^{0.56} = 0.00016 \text{ kmol/s m}^3 \text{ (kN/m}^2\text{)}$

For a very soluble gas such as NH₃, $k_G a \simeq K_G a$.

For NH₃ the liquid-film resistance will be small, and:

$$k_G a = K_G a = \underline{\underline{0.00016 \text{ kmol/s m}^3 \text{ (kN/m}^2\text{)}}$$

In early work on wetted-wall columns, MORRIS and JACKSON⁽²¹⁾ represented the experimental data for the mass transfer coefficient for the gas film h_D in a form similar to equation 12.25, though with slightly different indices, to give:

$$\frac{h_D}{u} = 0.04 \left[\frac{ud\rho}{\mu} \right]^{-0.25} \left[\frac{\mu}{\rho D_V} \right]^{-0.5} \left[\frac{P}{P_{Bm}} \right] \quad (12.26)$$

The velocity u of the gas is strictly the velocity relative to the surface of the falling liquid film, though little error is introduced if it is taken as the superficial velocity in the column.

Compounding of film coefficients

Assuming k_G is approximately proportional to $G^{0.8}$, equation 12.17 may be rearranged to give:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{\mathcal{H}}{k_L} = \frac{1}{\psi u^{0.8}} + \frac{\mathcal{H}}{k_L} \quad (12.27)$$

If k_L is assumed to be independent of the gas velocity, then a plot of $1/K_G$ against $1/u^{0.8}$ will give a straight line with a positive intercept on the vertical axis representing the liquid film resistance \mathcal{H}/k_L , as shown for ammonia and for sulphur dioxide in Figure 12.6. It may be seen that in each case a straight line is obtained. The lines for ammonia pass almost through the origin showing that the liquid film resistance is very small, although the line for sulphur dioxide gives a large intercept on the vertical axis, indicating a high value of the liquid film resistance.

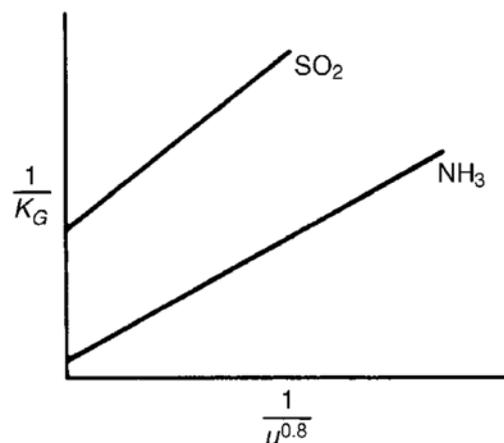


Figure 12.6. Plot of $1/K_G$ versus $1/u^{0.8}$ for ammonia and for sulphur dioxide

For a constant value of Re , the film thickness z_G should be independent of temperature, since $\mu/\rho D_V$ is almost independent of temperature. k_G will then vary as \sqrt{T} , because

$D_V \propto T^{3/2}$ and $k_G \propto D_V/T$. This is somewhat difficult to test accurately since the diffusivity in the liquid phase also depends on temperature. Thus, the data for sulphur dioxide, shown in Figure 12.6, qualitatively support the theory for different temperatures, although the increase in value of k_L masks the influence of temperature on k_G .

Example 12.2

A wetted-wall column is used for absorbing sulphur dioxide from air by means of a caustic soda solution. At an air flow of $2 \text{ kg/m}^2\text{s}$, corresponding to a Reynolds number of 5160, the friction factor $R/\rho u^2$ is 0.0200.

Calculate the mass transfer coefficient in $\text{kg SO}_2/\text{s m}^2 (\text{kN/m}^2)$ under these conditions if the tower is at atmospheric pressure. At the temperature of absorption the following values may be used:

The diffusion coefficient for $\text{SO}_2 = 0.116 \times 10^{-4} \text{ m}^2/\text{s}$, the viscosity of gas = 0.018 mNs/m^2 , and the density of gas stream = 1.154 kg/m^3 .

Solution

For wetted-wall columns, the data are correlated by:

$$\left(\frac{h_d}{u}\right) \left(\frac{P_{Bm}}{P}\right) \left(\frac{\mu}{\rho D}\right)^{0.56} = B' Re^{-0.17} = j_d \quad (\text{equation 12.25})$$

From Volume 1, Chapter 10: $j_d \simeq R/\rho u^2$

In this problem: $G' = 2.0 \text{ kg/m}^2\text{s}$, $Re = 5160$ and $R/\rho u^2 = 0.020$

$$D = 0.116 \times 10^{-4} \text{ m}^2/\text{s}, \quad \mu = 1.8 \times 10^{-5} \text{ Ns/m}^2, \quad \text{and } \rho = 1.154 \text{ kg/m}^3$$

Substituting these values gives:

$$\left(\frac{\mu}{\rho D}\right)^{0.56} = \left(\frac{1.8 \times 10^{-5}}{1.154 \times 0.116 \times 10^{-4}}\right)^{0.56} = 1.18$$

Thus:
$$\left(\frac{h_d}{u}\right) \left(\frac{P_{Bm}}{P}\right) = (0.020/1.18) = 0.0169$$

$$G' = \rho u = 2.0 \text{ kg/m}^2\text{s}$$

and:
$$u = (2.0/1.154) = 1.73 \text{ m/s}$$

Thus:
$$h_d(P_{Bm}/P) = (0.0169 \times 1.73) = 0.0293$$

d may be obtained from $d = Re\mu/\rho u = 0.046 \text{ m}$ (46 mm), which is the same order of size of wetted-wall column as that which was originally used in the research work.

$$k_G = \left(\frac{h_d}{RT}\right) \left(\frac{P_{Bm}}{P}\right)$$

$R = 8314 \text{ m}^3(\text{N/m}^2)/\text{K kmol}$ and T will be taken as 298 K, and hence:

$$k_G = [0.0293/(8314 \times 298)] = 1.18 \times 10^{-8} \text{ kmol/m}^2\text{s}(\text{N/m}^2)$$

$$= \underline{\underline{7.56 \times 10^{-4} \text{ kg SO}_2/\text{m}^2\text{s}(\text{kN/m}^2)}}$$

12.4.2. Coefficients in packed towers

The majority of published data on transfer coefficients in packed towers are for rather small laboratory units, and there is still some uncertainty in extending the data for use in industrial units. One of the great difficulties in correlating the performance of packed towers is the problem of assessing the effective wetted area for interphase transfer. It is convenient to consider separately conditions where the gas-film is controlling, and then where the liquid film is controlling. The general method of expressing results is based on that used for wetted-wall columns.

Gas-film controlled processes

The absorption of ammonia in water has been extensively studied by a number of workers. KOWALKE *et al.*⁽²²⁾ used a tower of 0.4 m internal diameter with a packing 1.2 m deep, and expressed their results as:

$$K_G a = \alpha G'^{0.8} \quad (12.28)$$

where K_G is expressed in $\text{kmol/s m}^2 (\text{kN/m}^2)$ and a is the interfacial surface per unit volume of tower (m^2/m^3). Thus $K_G a$ is a transfer coefficient based on unit volume of tower. G' is in kg/s m^2 , and varies with the nature of the packing and the liquid rate. It was noted that α increased with L' for values up to 1.1 kg/s m^2 , after which further increase gave no significant increase in $K_G a$. It was thought that the initial increase in the coefficient was occasioned by a more effective wetting of the packing. On increasing the liquid rate so that the column approached flooding conditions, it was found that $K_G a$ decreased. Other measurements by BORDEN and SQUIRES⁽²³⁾ and NORMAN⁽²⁴⁾ confirm the applicability of equation 12.28.

FELLINGER⁽²⁵⁾ used a 450 mm diameter column with downcomers and risers in an attempt to avoid the problem of determining any entrance or exit effects. Some of the results for H_{OG} are shown in Table 12.2, taken from Perry's Chemical Engineers' Handbook⁽²⁶⁾. Further discussion on the use of transfer units is included in Section 12.8.8 and in Chapter 11.

Table 12.2. Height of the transfer unit H_{OG} in metres

Raschig rings size (mm)	G' ($\text{kg/m}^2\text{s}$)	H_{OG} ($L' = 0.65 \text{ kg/m}^2\text{s}$)	H_{OG} ($L' = 1.95 \text{ kg/m}^2\text{s}$)
9.5	0.26	0.37	0.23
	0.78	0.60	0.32
25	0.26	0.40	0.22
	0.78	0.64	0.34
50	0.26	0.60	0.34
	0.78	1.04	0.58

MOLSTAD *et al.*⁽²⁷⁾ also measured the absorption of ammonia in water using a tower of 384 mm side packed with wood grids, or with rings or saddles, and obtained $K_G a$ by direct experiment. The value of $k_G a$ was then calculated from the following relation based on equation 12.17:

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{\mathcal{H}}{k_L a} \quad (12.29)$$

The simplest method of representing data for gas-film coefficients is to relate the Sherwood number $[(h_D d / D_V)(P_{Bm} / P)]$ to the Reynolds number (Re) and the Schmidt number $(\mu / \rho D_V)$. The indices used vary between investigators though VAN KREVELEN and HOFTIJZER⁽²⁸⁾ have given the following expression, which is claimed to be valid over a wide range of Reynolds numbers:

$$\frac{h_D d}{D_V} \frac{P_{Bm}}{P} = 0.2 Re^{0.8} \left(\frac{\mu}{\rho D_V} \right)^{0.33} \quad (12.30)$$

Later work suggests that 0.11 is a more realistic value for the coefficient.

SEMMELEBAUER⁽²⁹⁾ has recommended the following correlation for $100 < (Re)_G < 10,000$ and $0.01 \text{ m} < d_p < 0.05 \text{ m}$:

$$(Sh)_G = \beta (Re)_G^{0.59} (Sc)_G^{0.33} \quad (12.31)$$

where: $\beta = 0.69$ for Raschig rings and 0.86 for Berl saddles,

$$(Sh)_G = h_D d_p / D_G,$$

$$(Re)_G = G' d_p / \mu_G,$$

$$(Sc)_G = \mu_G / \rho_G D_G, \text{ and}$$

$$d_p = \text{packing size.}$$

Processes controlled by liquid-film resistance

The absorption of carbon dioxide, oxygen, and hydrogen in water are three examples in which most, if not all, of the resistance to transfer lies in the liquid phase. SHERWOOD and HOLLOWAY⁽³⁰⁾ measured values of $k_L a$ for these systems using a tower of 500 mm diameter packed with 37 mm rings. The results were expressed in the form:

$$\frac{k_L a}{D_L} = \beta \left[\frac{L'}{\mu_L} \right]^{0.75} \left[\frac{\mu_L}{\rho_L D_L} \right]^{0.50} \quad (12.32)$$

It may be noted that this equation has no term for characteristic length on the right-hand side and therefore it is not a dimensionally consistent equation. If values of $k_L a$ are plotted against value L' on logarithmic scales as shown in Figure 12.7, a slope of about 0.75 is obtained for values of L' 0.5–20 kg/s m². Beyond this value of L' , it was found that $k_L a$ tended to fall because the loading point for the column was reached. These values of $k_L a$ were found to be affected by the gas rate. Subsequently, COOPER *et al.*⁽³¹⁾ established that, at the high liquid rates and low gas rates used in practice, the transfer rates were much lower than given by equation 12.32. This was believed to be due to maldistribution at gas velocities as low as 0.03 m/s. The results of COOPER *et al.*⁽³¹⁾ and SHERWOOD and

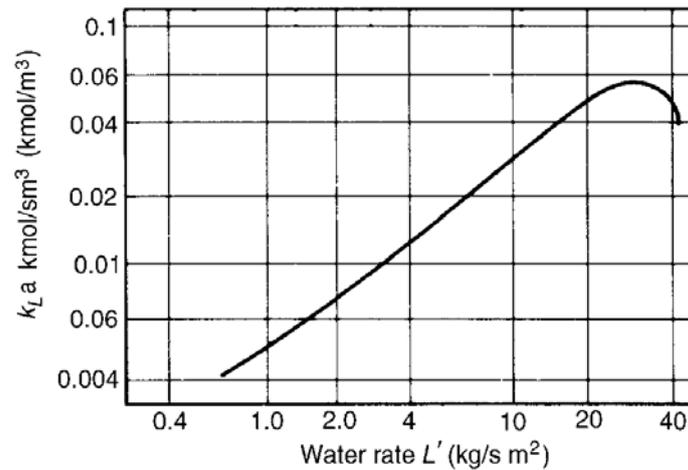


Figure 12.7. Variation of liquid-film coefficient with liquid flow for the absorption of oxygen in water

HOLLOWAY⁽³⁰⁾ are compared in Figure 12.8, where the height of the transfer unit H_{OL} is plotted against the liquid rate for various gas velocities.

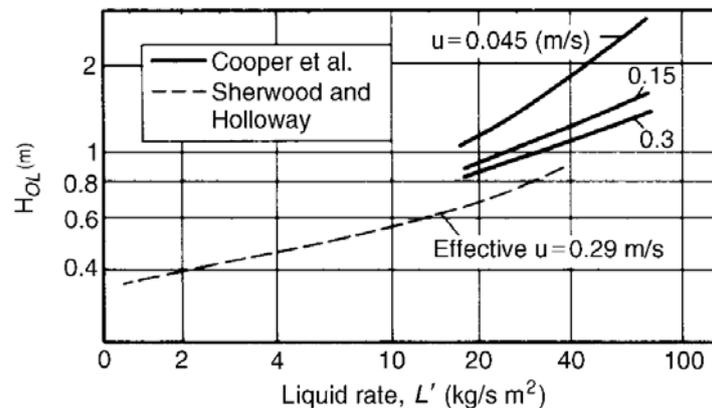


Figure 12.8. Effect of liquid rate on height of transfer unit H_{OL} . Comparison of the results of Sherwood and Holloway⁽³⁰⁾, and Cooper *et al.*⁽³¹⁾

In an equation similar to equation 12.31, SEMMELBAUER⁽²⁹⁾ produced the following correlation for the liquid film mass transfer coefficient k_L for $3 < Re_L < 3000$ and $0.01 \text{ m} < d_p < 0.05 \text{ m}$:

$$(Sh)_L = \beta' (Re)_L^{0.59} (Sc)_L^{0.5} (d_p^3 g \rho_L^2 / \mu_L^2)^{0.17} \quad (12.33)$$

where: $\beta' = 0.32$ and 0.25 for Raschig rings and Berl saddles, respectively.

$$(Sh)_L = k_L d_p / D_L,$$

$$(Re)_L = L' d_p / \mu_L, \text{ and}$$

$$(Sc)_L = \mu_L / \rho_L D_L.$$

NONHEBEL⁽³²⁾ emphasises that values of the individual film mass transfer coefficients obtained from this equation must be used with caution when designing large-scale towers and appropriately large safety factors should be incorporated.

12.4.3. Coefficients in spray towers

It is difficult to compare the performance of various spray towers since the type of spray distributor used influences the results. Data from HIXSON and SCOTT⁽³³⁾ and others show that $K_G a$ varies as $G'^{0.8}$, and is also affected by the liquid rate. More reliable data with spray columns might be expected if the liquid were introduced in the form of individual drops through a single jet into a tube full of gas. Unfortunately the drops tend to alter in size and shape and it is not possible to get the true interfacial area very accurately. This has been investigated by WHITMAN *et al.*⁽³⁴⁾, who found that k_G for the absorption of ammonia in water was about $0.035 \text{ kmol/s m}^2 \text{ (N/m}^2\text{)}$, compared with 0.00025 for the absorption of carbon dioxide in water.

Some values obtained by PIGFORD and PYLE⁽³⁵⁾ for the height of a transfer unit H_L for the stripping of oxygen from water are shown in Figure 12.9. For short heights, the efficiency of the spray chamber approximates closely to that of a packed tower although, for heights greater than 1.2 m, the efficiency of the spray tower drops off rather rapidly. Whilst it might be possible to obtain a very large active interface by producing small drops, in practice it is impossible to prevent these coalescing, and hence the effective interfacial surface falls off with height, and spray towers are not used extensively.

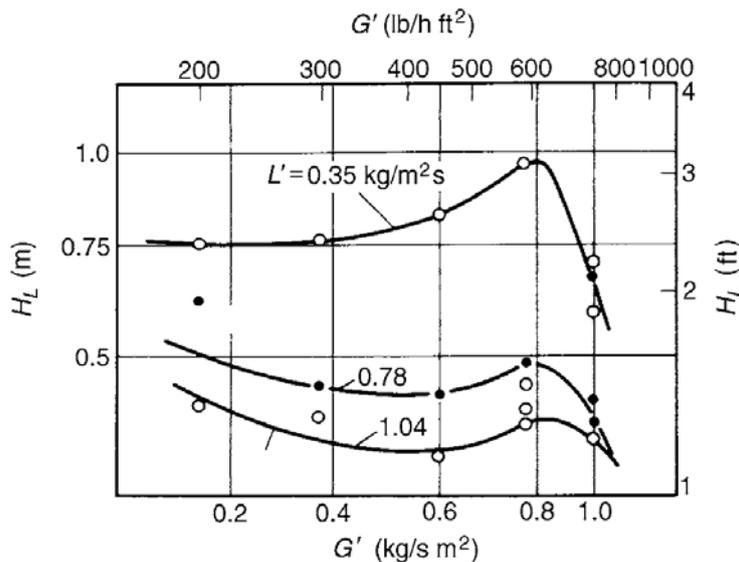


Figure 12.9. Height of the transfer unit H_L for stripping of oxygen from water in a spray tower

12.5. ABSORPTION ASSOCIATED WITH CHEMICAL REACTION

In the instances so far considered, the process of absorption of the gas in the liquid has been entirely a physical one. There are, however, a number of cases in which the gas, on absorption, reacts chemically with a component of the liquid phase⁽³⁶⁾. The topic of mass transfer accompanied by chemical reaction is treated in detail in Volume 1, Chapter 10.

In the absorption of carbon dioxide by caustic soda, the carbon dioxide reacts directly with the caustic soda and the process of mass transfer is thus made much more complicated. Again, when carbon dioxide is absorbed in an ethanolamine solution, there is direct chemical reaction between the amine and the gas. In such processes the conditions in the gas phase are similar to those already discussed, though in the liquid phase there is a liquid film followed by a reaction zone. The process of diffusion and chemical reaction may still be represented by an extension of the film theory by a method due to HATTA⁽³⁷⁾. In the case considered, the chemical reaction is irreversible and of the type in which a solute gas **A** is absorbed from a mixture by a substance **B** in the liquid phase, which combines with **A** according to the equation $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{AB}$. As the gas approaches the liquid interface, it dissolves and reacts at once with **B**. The new product **AB**, thus formed, diffuses towards the main body of the liquid. The concentration of **B** at the interface falls; this results in diffusion of **B** from the bulk of the liquid phase to the interface. Since the chemical reaction is rapid, **B** is removed very quickly, so that it is necessary for the gas **A** to diffuse through part of the liquid film before meeting **B**. There is thus a zone of reaction between **A** and **B** which moves away from the gas-liquid interface, taking up some position towards the bulk of the liquid. The final position of this reaction zone will be such that the rate of diffusion of **A** from the gas-liquid interface is equal to the rate of diffusion of **B** from the main body of the liquid. When this condition has been reached, the concentrations of **A**, **B**, and **AB** may be indicated as shown in Figure 12.10, where the concentrations are shown as ordinates and the positions of a plane relative to the interface as abscissae. In this Figure, the plane of the interface between gas and liquid is shown by U, the reaction zone by R, and the outer boundary of liquid film by S. Then **A** diffuses through the gas film as a result of the driving force $(P_{AG} - P_{Ai})$ and diffuses to the reaction zone as a result of the driving force C_{Ai} in the liquid phase. The component **B** diffuses from the main body of the liquid to the reaction zone under a driving force q , and the non-volatile product **AB** diffuses back to the main bulk of the liquid under a driving force $(m - n)$.

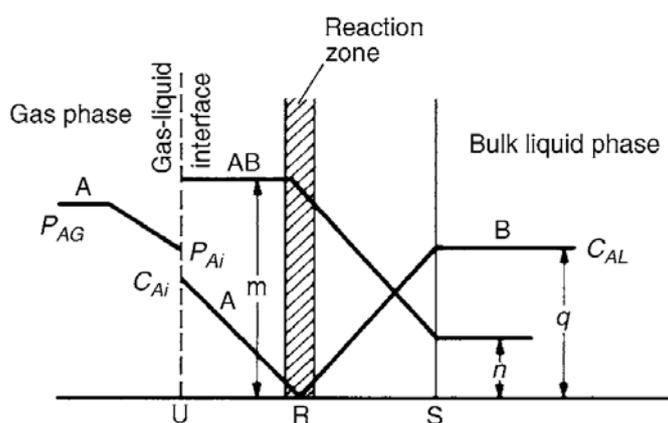


Figure 12.10. Concentration profile for absorption with chemical reaction

The difference between a physical absorption, and one in which a chemical reaction occurs, can also be shown by Figures 12.11a and 12.11b, taken from a paper by VAN KREVELEN and HOFTIJZER⁽²⁸⁾. Figure 12.11a shows the normal concentration profile for

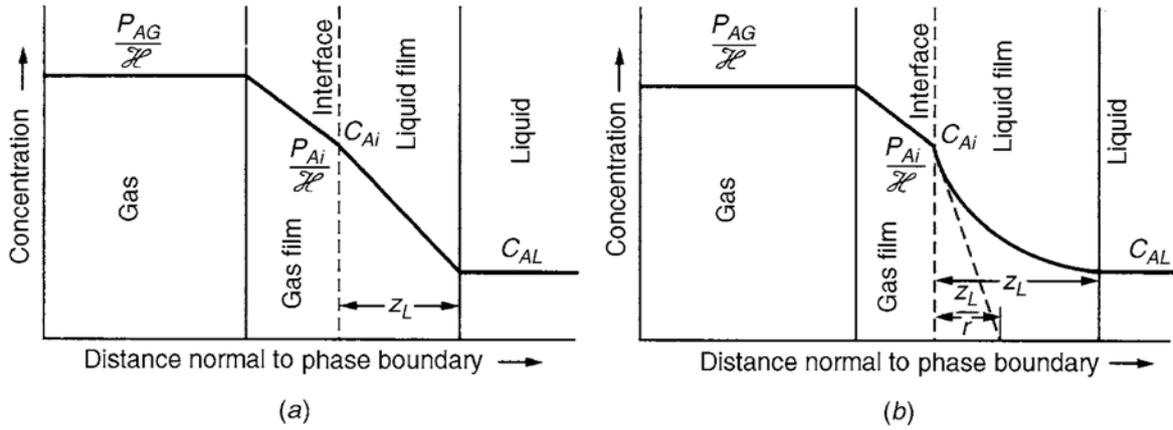


Figure 12.11. Concentration profiles for absorption (a) without chemical reaction, (b) with chemical reaction. The scales for concentration in the two phases are not the same and are chosen so that P_{Ai}/\mathcal{H} in the gas phase and C_{Ai} for the liquid phase are at the same position in the diagrams

physical absorption whilst Figure 12.11b shows the profile modified by the chemical reaction. For transfer in the gas phase:

$$N'_A = k_G(P_{AG} - P_{Ai}) \quad (12.34)$$

and in the liquid phase:

$$N'_A = k_L(C_{Ai} - C_{AL}) \quad (12.35)$$

The effect of the chemical reaction is to accelerate the removal of **A** from the interface, and supposing that it is now r times as great then:

$$N''_A = rk_L(C_{Ai} - C_{AL}) \quad (12.36)$$

In Figure 12.11a, the concentration profile through the liquid film of thickness z_L is represented by a straight line such that $k_L = D_L/z_L$. In b, component **A** is removed by chemical reaction, so that the concentration profile is curved. The dotted line gives the concentration profile if, for the same rate of absorption, **A** were removed only by diffusion. The effective diffusion path is $1/r$ times the total film thickness z_L .

Thus:

$$N''_A = \frac{rD_L}{z_L}(C_{Ai} - C_{AL}) = rk_L(C_{Ai} - C_{AL}) \quad (12.37)$$

VAN KREVELEN and HOFTYZER⁽²⁸⁾ showed that the factor r may be related to C_{Ai} , D_L , k_L , to the concentration of **B** in the bulk liquid C_{BL} , and to the second-order reaction rate constant k_2 for the absorption of CO_2 in alkaline solutions. Their relationship is shown in Figure 12.12, in which r , that is $N''_A/k_L C_{Ai}$, is plotted against $(k_2 D_L C_{BL})^{1/2}/k_L$ for various values of C_{BL}/iC_{Ai} , where i is the number of kmol of **B** combining with 1 kmol of **A**.

Figure 12.2 illustrates three conditions:

- (a) If k_2 is very small, $r \simeq 1$, and conditions are those of physical absorption.
- (b) If k_2 is very large, $r \simeq C_{BL}/iC_{Ai}$, and the rate of the process is determined by the transport of **B** towards the phase boundary.

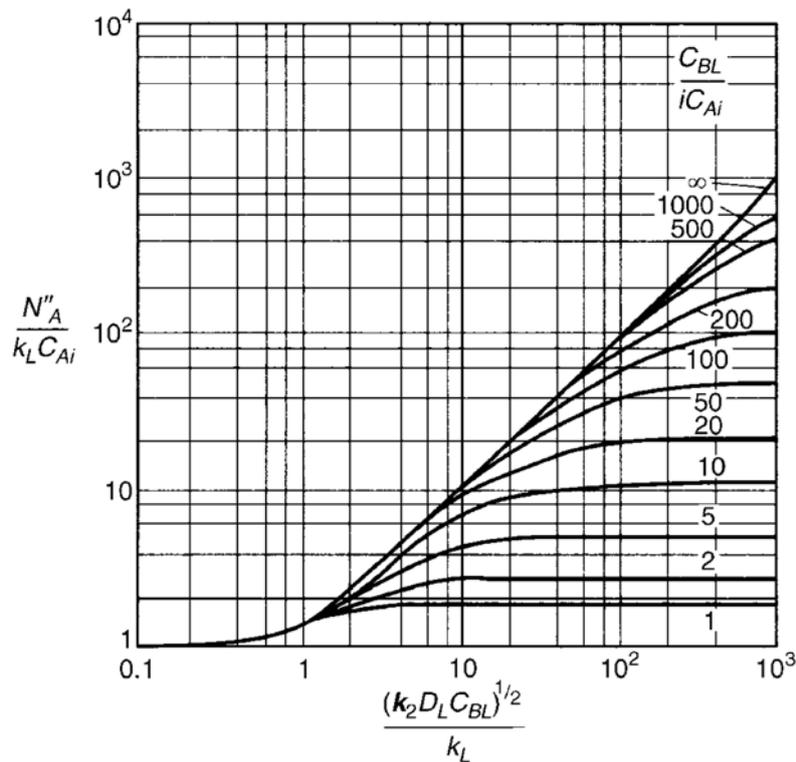


Figure 12.12. $N''_A/k_L C_{Ai}$ versus $(k_2 D_L C_{BL})^{1/2}/k_L$ for various values of C_{BL}/iC_{Ai}

- (c) At moderate values of k_2 , $r \simeq (j D_L C_{BL})^{1/2}/k_L$, and the rate of the process is determined by the rate of the chemical reaction.

Thus, from equation 12.37:

$$N''_A = k_L(C_{Ai} - C_{AL}) \frac{(k_2 D_L C_{BL})^{1/2}}{k_L} = (C_{Ai} - C_{AL})(k_2 D_L C_{BL})^{1/2} \quad (12.38)$$

and the controlling parameter is now k_2 .

The results of this work have been confirmed by NIJSING, HENDRIKSZ, and KRAMERS⁽³⁸⁾.

As an illustration of combined absorption and chemical reaction, the results of TEPE and DODGE⁽³⁹⁾ on the absorption of carbon dioxide by sodium hydroxide solution may be considered. A 150 mm diameter tower filled to a depth of 915 mm with 12.5 mm carbon Raschig rings was used. Some of the results are indicated in Figure 12.13. $K_G a$ increases rapidly with increasing sodium hydroxide concentration up to a value of about 2 kmol/m³. Changes in the gas rate were found to have negligible effect on $K_G a$, indicating that the major resistance to absorption was in the liquid phase. The influence of the liquid rate was rather low, and was proportional to $L^{0.28}$. It may be assumed that, in this case, the final rate of the process is controlled by the resistance to diffusion in the liquid, by the rate of the chemical reaction, or by both together.

CRYDER and MALONEY⁽⁴⁰⁾ presented data on the absorption of carbon dioxide in diethanolamine solution, using a 200 mm tower filled with 20 mm rings, and some of their data are shown in Figure 12.14. The coefficient $K_G a$ is found to be independent of

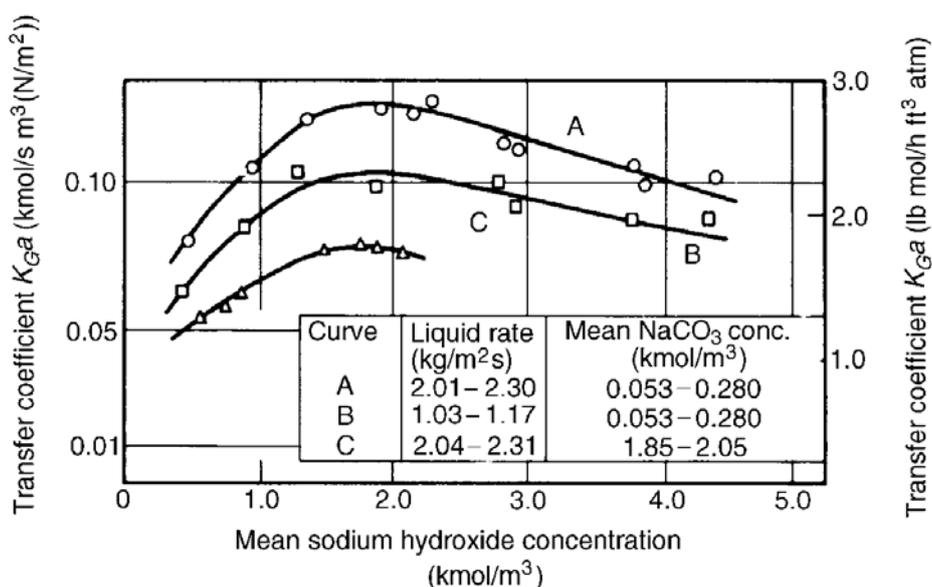


Figure 12.13. Absorption of carbon dioxide in sodium hydroxide solution $G' = 0.24-0.25 \text{ kg/m}^2\text{s}$, temperature = 298 K

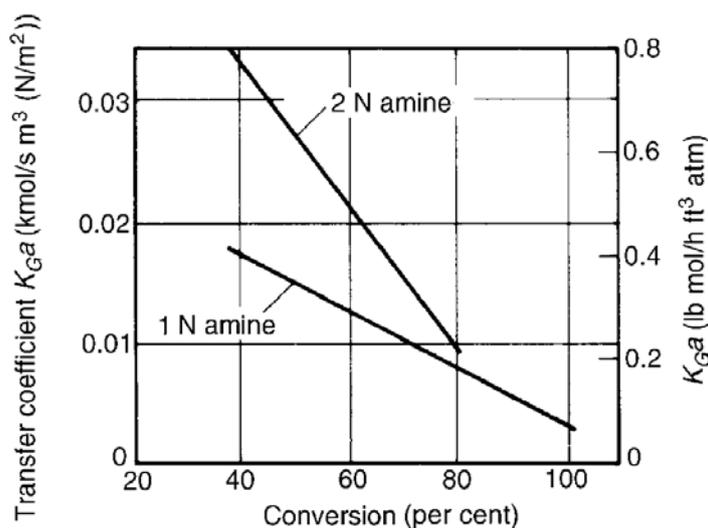


Figure 12.14. Absorption of carbon dioxide in diethanolamine solutions. Liquid rate = $1.85 \text{ kg/m}^2\text{s}$

the gas rate but to increase with the liquid rate, as expected in a process controlled by the resistance in the liquid phase.

It is difficult to deduce the size of tower required for an absorption combined with a chemical reaction, and a laboratory scale experiment should be carried out in all cases. STEPHENS and MORRIS⁽⁴¹⁾ have used a small disc-type tower illustrated in Figure 12.15 for preliminary experiments of this kind. It was found that a simple wetted-wall column was unsatisfactory where chemical reactions took place. In this unit a series of discs, supported by means of a wire, was arranged one on top of the other as shown.

The absorption of carbon dioxide into aqueous amine solutions has been investigated by DANCKWERTS and MCNEIL⁽⁴²⁾ using a stirred cell. It was found that the reaction proceeded

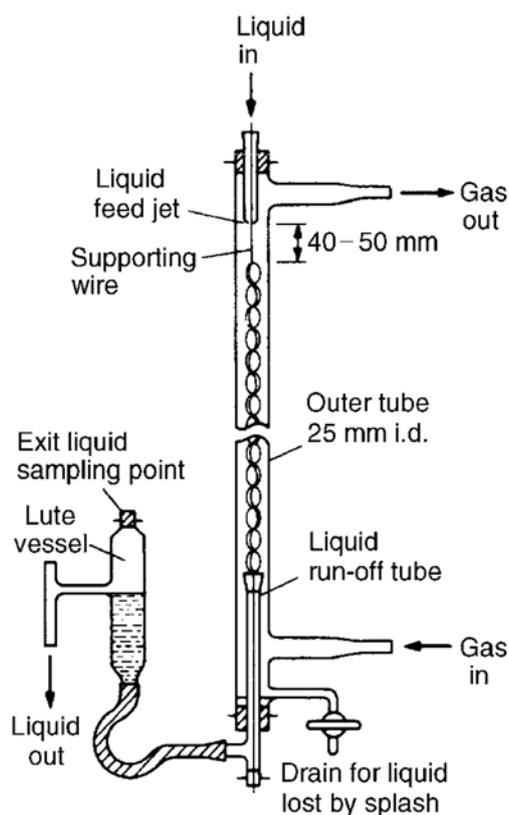


Figure 12.15. Small disc-tower for absorption tests

in two stages: first a fast reaction to give amine carbamate, and secondly a slow reaction in the bulk of the liquid in which the carbamate was partially hydrolysed to bicarbonate. The use of sodium arsenite as catalyst considerably accelerated this second reaction, showing that the overall capacity of an absorber could be substantially increased by a suitable catalyst.

A comprehensive review of work on the absorption of carbon dioxide by alkaline solutions has been carried out by DANCKWERTS and SHARMA⁽⁴³⁾ who applied results of research to the design of industrial scale equipment. Subsequently, SAHAY and SHARMA⁽⁴⁴⁾ showed that the mass transfer coefficient may be correlated with the gas and liquid rates and the gas and liquid compositions by:

$$K_G a = \text{const. } L'^{a_1} G'^{a_2} \exp(a_3 F' + a_4 y) \quad (12.39)$$

where: a_1, a_2, a_3, a_4 are experimentally determined constants,

F' = fractional conversion of the liquid, and

y = mole fraction of CO_2 in the gas.

ECKERT⁽⁴⁵⁾, by using the same reaction, determined the mass transfer performance of packings in terms of $K_G a$ as:

$$K_G a = \frac{N}{V(\Delta P_A)_{\text{lm}}} \quad (12.40)$$

where: N = number of moles of CO_2 absorbed,
 V = packed volume, and
 $(\Delta P_A)_{\text{lm}}$ = log mean driving force.

Data obtained from this work are limited by the conditions under which they were obtained. It is both difficult and dangerous to extrapolate over the entire range of conditions encountered on a full-scale plant.

12.6. ABSORPTION ACCOMPANIED BY THE LIBERATION OF HEAT

In some absorption processes, especially where a chemical reaction occurs, there is a liberation of heat. This generally gives rise to an increase in the temperature of the liquid, with the result that the position of the equilibrium curve is adversely affected.

In the case of plate columns, a heat balance may be performed over each plate and the resulting temperature determined. For adiabatic operation, where no heat is removed from the system, the temperature of the streams leaving the absorber will be higher than those entering, due to the heat of solution. This rise in temperature lowers the solubility of the solute gas so that a large value of L_m/G_m and a larger number of trays will be required than for isothermal operation.

For packed columns, the temperature rise will affect the equilibrium curve, and differential equations for heat and mass transfer, together with heat and mass balances, must be integrated numerically. An example of this procedure is given in Volume 1, Chapter 13, for the case of water cooling. For gas absorption under non-isothermal conditions, reference may be made to specialist texts^(46,47) for a detailed description of the methods available. As an approximation, it is sometimes assumed that all the heat evolved is taken up by the liquid, and that temperature rise of the gas may be neglected. This method gives an overestimate of the rise in temperature of the liquid and results in the design of a tower which is taller than necessary. Figure 12.16 shows the effect of the temperature rise on the equilibrium curve for an adiabatic absorption process of ammonia in water. If the amount of heat liberated is very large, it may be necessary to cool the liquid. This is most conveniently done in a plate column, either with heat exchangers connected between consecutive plates, or with cooling coils on the plate, as shown in Figure 12.17.

The overall heat transfer coefficient between the gas–liquid dispersion on the tray and the cooling medium in the tubes is dependent upon the gas velocity, as pointed out by POLL and SMITH⁽⁴⁸⁾, but is usually in the range 500–2000 W/m² K.

With packed towers it is considerably more difficult to arrange for cooling, and it is usually necessary to remove the liquid stream at intervals down the column and to cool externally. COGGAN and BOURNE⁽⁴⁹⁾ have presented a computer programme to enable the economic decision to be made between an adiabatic absorption tower, or a smaller isothermal column with interstage cooling.

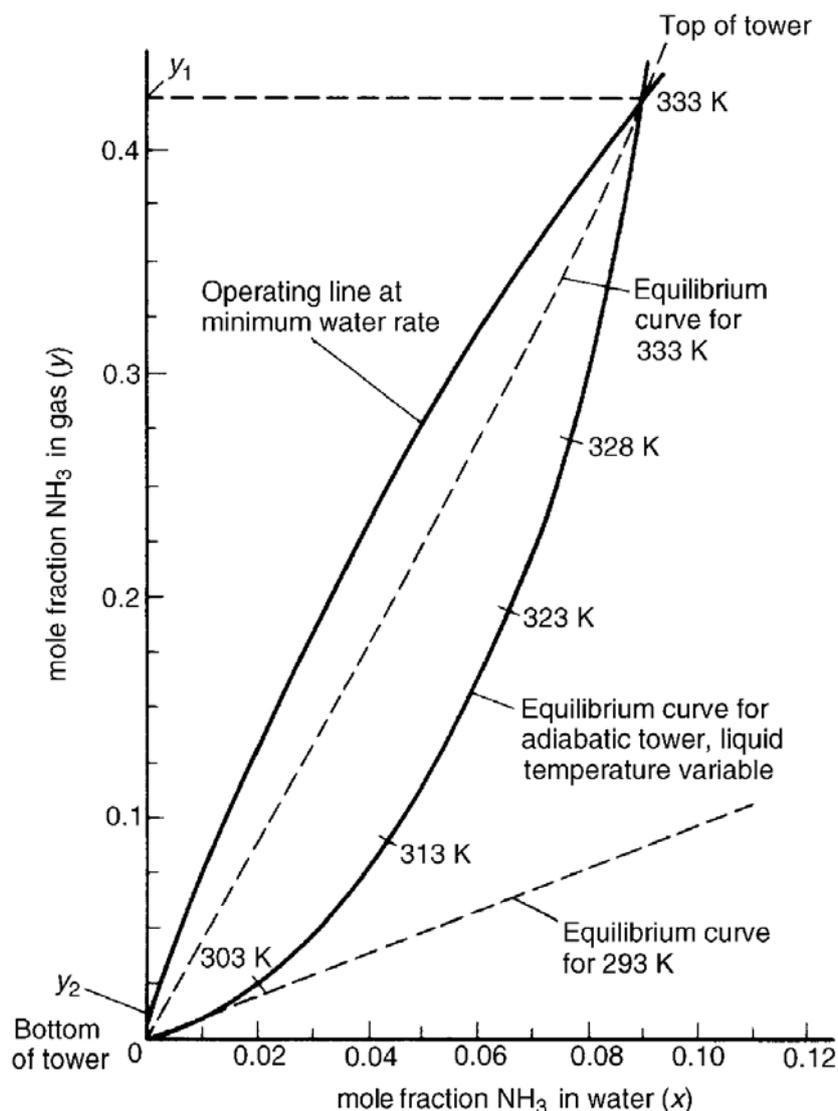


Figure 12.16. Equilibrium curve modified to allow for the heat of solution of the solute⁽⁴⁶⁾

12.7. PACKED TOWERS FOR GAS ABSORPTION

From the analysis given already of the diffusional nature of absorption, one of the outstanding requirements is to provide as large an interfacial area of contact as possible between the phases. For this purpose, columns similar to those used for distillation are suitable. However, whereas distillation columns are usually tall and thin absorption columns are more likely to be short and fat. In addition, equipment may be used in which gas is passed into a liquid which is agitated by a stirrer. A few special forms of units have also been used, although it is the packed column which is most frequently used for gas absorption applications.

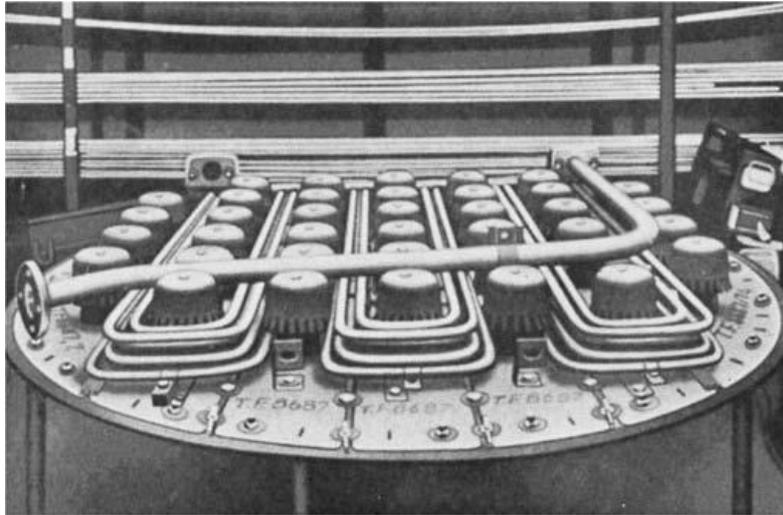


Figure 12.17. Glitsch “truss type” bubble-tray in stainless steel for a 1.9 m absorption column

12.7.1. Construction

The essential features of a packed column, as discussed in Chapter 4, are the shell, the arrangements for the gas and liquid inlets and outlets and the packing with its necessary supporting and redistributing systems. Reference may be made to Chapter 4 and to Volume 6 for details of these aspects, whilst this section is largely concerned with the determination of the height of packing for a particular duty. In installations where the gas is fed from a previous stage of a process where it is under pressure, there is no need to use a blower for the transfer of the gas through the column. When this is not the case, a simple blower is commonly used, and such blowers have been described in Volume 1, Chapter 8. The pressure drop across the column may be calculated by the methods presented in Chapter 4 of this volume and the blower sized accordingly. A pressure drop exceeding 30 mm of water per metre of packing is said to improve gas distribution though process conditions may not permit a figure as high as this. The packed height should not normally exceed 6 m in any section of the tower and for some packings a much lower height must be used.

In the design of an absorption tower it is necessary to take into account the characteristics of the packing elements and the flow behaviour discussed in Chapter 4, together with the considerations given in the following sections concerning the performance of columns under operating conditions.

12.7.2. Mass transfer coefficients and specific area in packed towers

Traditional methods of assessing the capacity of tower packings, which involve the use of the specific surface area S and the voidage e , developed from the fact that these

properties could be readily defined and measured for a packed bed of granular material such as granite, limestone, and coke which were some of the earliest forms of tower packings. The values of S and e enabled a reasonable prediction of hydraulic performance to be made. With the introduction of Raschig rings and other specially shaped packings, it was necessary to introduce a basis for comparing their relative efficiencies. Although the commonly published values of specific surface area S provide a reasonable basis of comparison, papers such as that by SHULMAN *et al.*⁽⁵⁰⁾ showed that the total area offered by Raschig rings was not used, and varied considerably with hydraulic loading.

Further evidence of the importance of the wetted fraction of the total area came with the introduction of the Pall type ring. A Pall ring having the same surface area as a Raschig ring is up to 60 per cent more efficient, though many still argue the relative merits of packings purely on the basis of surface area.

The selection of a tower packing is based on its hydraulic capacity, which determines the required cross-sectional area of the tower, and the efficiency, $K_G a$ typically, which governs the packing height. Here a is the area of surface per unit volume of column and is therefore equal to $S(1 - e)$. Table 12.3⁽⁵¹⁾ shows the capacity of the commonly available tower packings relative to 25 mm Raschig rings, for which a considerable amount of information is published in the literature. The table lists the packings in order of relative efficiency, $K_G a$, evaluated at the same approach to the hydraulic capacity limit determined by flooding in each case.

12.7.3. Capacity of packed towers

The drop in pressure for the flow of gas and liquid over packings is discussed in Chapter 4. It is important to note that, during operation, the tower does not reach flooding conditions. In addition, every effort should be made to have as high a liquid rate as possible, in order to attain satisfactory wetting of the packing.

With low liquid rates, the whole of the surface of the packing is not completely wetted. This may be seen very readily by allowing a coloured liquid to flow over packing contained in a glass tube. From the flow patterns, it is obvious how little of the surface is wetted until the rate is quite high. This difficulty of wetting can sometimes be overcome by having considerable recirculation of the liquid over the tower, although in other cases, such as vacuum distillation, poor wetting will have to be accepted because of the low volume of liquid available. In selecting a packing, it is desirable to choose the form which will give as near complete wetting as possible. The minimum liquid rate below which the packing will no longer perform satisfactorily is known as the minimum wetting rate, discussed in Chapter 4.

The following treatment is a particular application of the more general approach adopted in Volume 1, Chapter 10.

Figure 12.18 illustrates the conditions that occur during the steady operation of a countercurrent gas–liquid absorption tower. It is convenient to express the concentration of the streams in terms of moles of solute gas per mole of inert gas in the gas phase, and as moles of solute gas per mole of solute free liquid in the liquid phase. The actual area of interface between the two phases is not known, and the term a is introduced as the interfacial area per unit volume of the column. On this basis the general equation, 12.13,

Table 12.3. Capacity of commonly available packings relative to 25 mm Raschig rings⁽⁵¹⁾

Relative K_{Ga}	Raschig rings	Traditional saddles	Pall rings	Ceramic Pall rings	Ceramic cascade mini ring ⁽³⁾	Super Intalox [®] saddles	Hypak [®]	Tellerettes [®]	Cascade mini-ring [®]
Materials available for this relative K_{Ga}	Ceramic	Ceramic Plastic (P)	Metal (M)	Ceramic	Ceramic	Ceramic Plastic	Metal	Plastic	Metal (M) Plastic (P)
0.6-0.7	75 mm								
0.7-0.8	50 mm								
0.8-0.9	37 mm								
0.9-1.0	25 mm								
1.0-1.1	12 mm	75 mm	87 mm		No. 5	No. 3	No. 3	Size L	
1.1-1.2		50 mm	50 mm				No. 3		
1.2-1.3		37 mm	50 mm		No. 3	No. 2	No. 2		
1.3-1.4		25 mm	37 mm						
1.4-1.5				50 mm					No. 4 (M)
1.5-1.6			25 mm	37 mm					No. 3 (P)
1.6-1.7			25 mm	25 mm	No. 2	No. 1	No. 1	Size S	No. 3 (M)
1.7-1.8			16 mm						No. 2 (P)
1.8-1.9									No. 2 (M)
1.9-2.0									No. 1 (P)
2.0-2.1									
2.1-2.2									No. 1 (M)

Note:

Relative K_{Ga} valid for all systems controlled by mass transfer coefficient (K_G) and wetted area (a) per unit volume of column. Some variation should be expected when liquid *reaction* rate is controlling (not liquid *diffusion* rate). In these cases liquid hold-up becomes more important. In general a packing having high liquid hold-up which is clearly greater than that in the falling film has poor capacity.

Gas capacity before hydraulic limit (flooding) relative to 25 mm Raschig rings (also approx. the reciprocal of tower cross-sectional area relative to 25 mm Raschig rings for the same pressure drop throughout loading range). All relative capacity figures are valid for the same liquid to gas mass rate ratio:

- (1) Trade Mark of Norton Company, U.S.A. (Hydronyl U.K.).
- (2) Trade Mark of Ceilcote Company.
- (3) Trade Mark of Mass Transfer Ltd. (& Inc.).

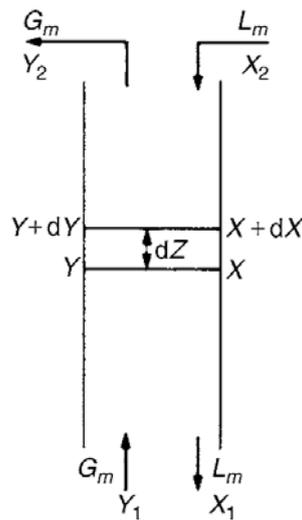


Figure 12.18. Countercurrent absorption tower

for mass transfer can be written as:

$$\begin{aligned} N'_A A dZ a &= k_G a (P_{AG} - P_{Ai}) A dZ \\ &= k_L a (C_{Ai} - C_{AL}) A dZ \end{aligned} \quad (12.41)$$

where: N'_A = kmol of solute absorbed per unit time and unit interfacial area,
 a = surface area of interface per unit volume of column,
 A = cross-sectional area of column, and
 Z = height of packed section.

$$\text{The interfacial area for transfer} = a dV = a A dZ \quad (12.42)$$

12.7.4. Height of column based on conditions in the gas film

If G_m = moles of inert gas/(unit time) (unit cross-section of tower),
 L_m = moles of solute-free liquor/(unit time) (unit cross-section of tower),
 Y = moles of solute gas **A**/mole of inert gas **B** in gas phase, and
 X = moles of solute **A**/mole of inert solvent in liquid phase.

and at any plane at which the molar ratios of the diffusing material in the gas and liquid phases are Y and X , then over a small height dZ , the moles of gas leaving the gas phase will equal the moles taken up by the liquid.

$$\text{Thus:} \quad AG_m dY = AL_m dX \quad (12.43)$$

$$\text{But:} \quad G_m A dY = N'_A (a dV) = k_G a (P_{Ai} - P_{AG}) A dZ \quad (12.44)$$

It may be noted that, in a gas absorption process, gas and liquid concentrations will decrease in the upwards direction and both dX and dY will be negative.

Since:

$$P_{AG} = \frac{Y}{1+Y}P$$

$$G_m dY = k_G a P \left[\frac{Y_i}{1+Y_i} - \frac{Y}{1+Y} \right] dZ$$

$$= k_G a P \left[\frac{Y_i - Y}{(1+Y)(1+Y_i)} \right] dZ$$

Hence the height of column Z required to achieve a change in Y from Y_1 at the bottom to Y_2 at the top of the column is given by:

$$\int_0^Z dZ = Z = \frac{G_m}{k_G a P} \int_{Y_1}^{Y_2} \frac{(1+Y)(1+Y_i) dY}{Y_i - Y} \quad (12.45)$$

which for dilute mixtures may be written as:

$$Z = \frac{G_m}{k_G a P} \int_{Y_1}^{Y_2} \frac{dY}{Y_i - Y} \quad (12.46)$$

In this analysis it has been assumed that k_G is a constant throughout the column, and provided the concentration changes are not too large this will be reasonably true.

12.7.5. Height of column based on conditions in liquid film

A similar analysis may be made in terms of the liquid film. Thus from equations 12.41 and 12.42:

$$AL_m dX = k_L a (C_{Ai} - C_{AL}) A dZ \quad (12.47)$$

where the concentrations C are in terms of moles of solute per unit volume of liquor. If $C_T = (\text{moles of solute} + \text{solvent}) / (\text{volume of liquid})$, then:

$$\frac{C_A}{C_T - C_A} = \frac{\text{moles of solute}}{\text{moles of solvent}} = X$$

whence:

$$C_A = \frac{X}{1+X} C_T \quad (12.48)$$

The transfer equation (12.47) may now be written as:

$$L_m dX = k_L a C_T \left[\frac{X}{1+X} - \frac{X_i}{1+X_i} \right] dZ$$

$$= k_L a C_T \left[\frac{X - X_i}{(1+X_i)(1+X)} \right] dZ$$

Thus:

$$\int_0^Z dZ = Z = \frac{L_m}{k_L a C_T} \int_{X_1}^{X_2} \frac{(1+X_i)(1+X) dX}{X - X_i} \quad (12.49)$$

and for dilute concentrations this gives:

$$Z = \frac{L_m}{k_L a C_T} \int_{X_1}^{X_2} \frac{dX}{X - X_i} \quad (12.50)$$

where C_T and k_L have been taken as constant over the column.

12.7.6. Height based on overall coefficients

If the driving force based on the gas concentration is written as $(Y - Y_e)$ and the overall gas transfer coefficient as K_G , then the height of the tower for dilute concentrations becomes:

$$Z = \frac{G_m}{K_G a P} \int_{Y_1}^{Y_2} \frac{dY}{Y_e - Y} \quad (12.51)$$

or in terms of the liquor concentration as:

$$Z = \frac{L_m}{K_L a C_T} \int_{X_1}^{X_2} \frac{dX}{X - X_e} \quad (12.52)$$

Equations for dilute concentrations

As the mole fraction is approximately equal to the molar ratio at dilute concentrations then considering the gas film:

$$Z = \frac{G_m}{K_G a P} \int_{Y_1}^{Y_2} \frac{dY}{Y_e - Y} = \frac{G_m}{K_G a P} \int_{y_1}^{y_2} \frac{dy}{y_e - y} \quad (12.53)$$

and considering the liquid film:

$$Z = \frac{L_m}{K_L a C_T} \int_{X_1}^{X_2} \frac{dX}{X - X_e} = \frac{L_m}{K_L a C_T} \int_{x_1}^{x_2} \frac{dx}{x - x_e} \quad (12.54)$$

12.7.7. The operating line and graphical integration for the height of a column

Taking a material balance on the solute from the bottom of the column to any plane where the mole ratios are Y and X gives for unit area of cross-section:

$$G_m(Y_1 - Y) = L_m(X_1 - X) \quad (12.55)$$

or:
$$Y_1 - Y = \frac{L_m}{G_m}(X_1 - X) \quad (12.56)$$

This is the equation of a straight line of slope L_m/G_m , which passes through the point (X_1, Y_1) . It may be seen by making a material balance over the whole column that the same line passes through the point (X_2, Y_2) . This line, known as the operating line,

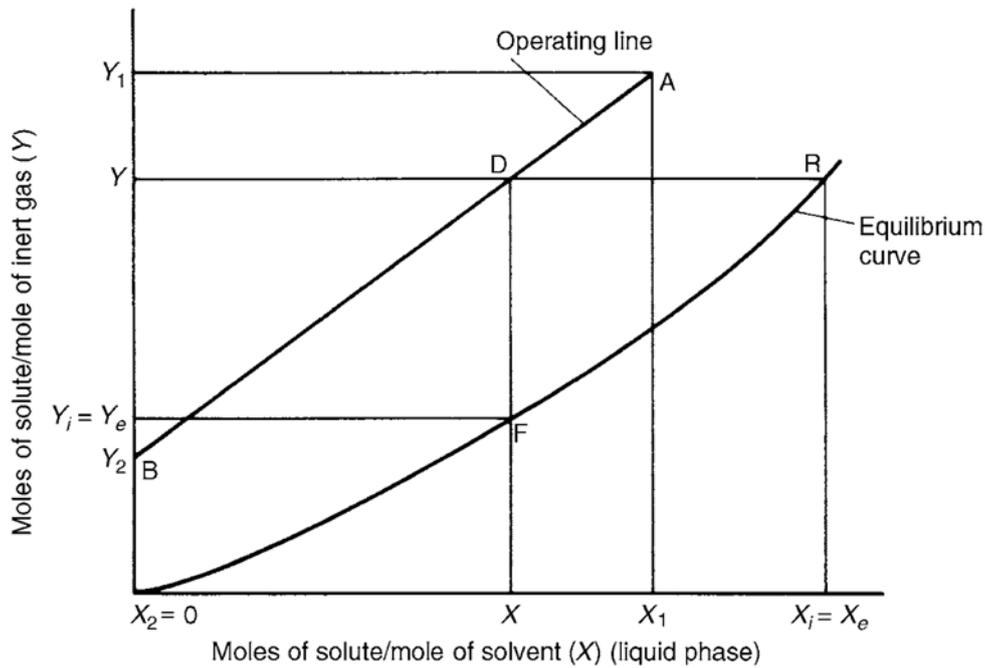


Figure 12.19. Driving force in gas and liquid-film controlled processes. The Figure shows the operating line BDA and the equilibrium curve FR

represents the conditions at any point in the column. It is similar to the operating line used in Chapter 11. Figure 12.19 illustrates typical conditions for the case of moist air and sulphuric acid or caustic soda solution, where the main resistance lies in the gas phase.

The equilibrium curve is represented by the line FR, and the operating line is given by AB, A corresponding to the concentrations at the bottom of the column and B to those at the top of the column. D represents the condition of the bulk of the liquid and gas at any point in the column, and has coordinates X and Y. Then, if the gas film is controlling the process, Y_i equals Y_e , and is given by a point F on the equilibrium curve, with coordinates X and Y_i . The driving force causing transfer is then given by the distance DF. It is therefore possible to evaluate the expression:

$$\int_{Y_1}^{Y_2} \frac{dY}{Y_i - Y}$$

by selecting values of Y, reading off from the Figure the corresponding values of Y_i , and thus calculating $1/(Y_i - Y)$. It may be noted that, for gas absorption, $Y > Y_i$ and $Y_i - Y$ and dY in the integral are both negative.

If the liquid film controls the process, X_i equals X_e and the driving force $X_i - X$ is given in Figure 12.19 by the line DR. The evaluation of the integral:

$$\int_{X_1}^{X_2} \frac{dX}{X - X_i}$$

may be effected in the same way as for the gas film.

Special case when equilibrium curve is a straight line

If over the range of concentrations considered the equilibrium curve is a straight line, it is permissible to use a mean value of the driving force over the column. For dilute concentrations, over a small height dZ of column, the absorption is given by:

$$N'_A A a dZ = G_m A dy = K_G a A P (y_e - y) dZ \quad (12.57)$$

If: $y_e = mx + c$ (12.58)

then: $y_{e2} = mx_2 + c$

and: $y_{e1} = mx_1 + c$

so that: $m = \frac{y_{e1} - y_{e2}}{x_1 - x_2}$ (12.59)

Further, taking a material balance over the lower portion of the columns gives:

$$L_m(x_1 - x) = G_m(y_1 - y)$$

and: $x = x_1 - \frac{G_m}{L_m}(y_1 - y)$ (12.60)

From equation 12.57:

$$\int_0^Z \frac{K_G a P}{G_m} dZ = \int_{y_1}^{y_2} \frac{dy}{y_e - y} \quad (12.61)$$

$$= \int_{y_1}^{y_2} \frac{dy}{m[x_1 + (G_m/L_m)(y - y_1)] + c - y}$$

(from equations 12.58 and 12.60)

$$= \frac{1}{1 - (mG_m/L_m)} \ln \frac{mx_1 + c - y_1}{y_2 - m[x_1 + (G_m/L_m)(y_2 - y_1)] - c}$$

$$= \frac{1}{1 - \frac{y_{e1} - y_{e2}}{x_1 - x_2} \cdot \frac{x_1 - x_2}{y_1 - y_2}} \ln \frac{y_{e1} - y_1}{y_{e1} - y_{e2} - \left(\frac{y_{e1} - y_{e2}}{x_1 - x_2} \frac{x_1 - x_2}{y_1 - y_2} y_1 - y_2 \right)}$$

(from equations 12.58, 12.59, and 12.60)

$$= \frac{y_1 - y_2}{(y - y_e)_1 - (y - y_e)_2} \ln \frac{(y - y_e)_1}{(y - y_e)_2}$$

$$= \frac{y_1 - y_2}{(y - y_e)_{lm}}$$

where $(y - y_e)_{lm}$ is the logarithmic mean value of $y - y_e$.

Substituting in equation 12.61:

$$\frac{K_G a P}{G_m} Z = \frac{y_1 - y_2}{(y - y_e)_{lm}}$$

Thus: $aAZN'_A = G_m(y_1 - y_2)A = K_G a A P (y - y_e)_{lm} Z$ (12.62)

and in terms of mole ratios:

$$aAZN'_A = G_m(Y_1 - Y_2)A = K_G aAP(Y - Y_e)_{lm}Z \quad (12.63)$$

Thus, the logarithmic mean of the driving forces at the top and the bottom of the column may be used.

For concentrated solutions:

$$aAZN'_A = G_m(Y_1 - Y_2)A = K_G aA\phi P(Y - Y_e)_{lm}Z \quad (12.64)$$

It is necessary to introduce the factor ϕ since Y is not directly proportional to P . The value of ϕ may be found from the relation:

$$\phi Y = \frac{Y}{1 + Y} \quad (12.65)$$

from which $\phi = 1/(1 + Y)$. Although the value of ϕ will change slightly over the column, a mean value will generally be acceptable.

It is of interest to note from Figure 12.20, that, as long as the ratio k_L/k_G remains constant (that is, if the slope of DE is constant), then the ratio of DQ, the driving force through the gas phase, divided by DF, the driving force assuming all the resistance to be in the gas phase, will be a constant. Thus, the use of the driving force DF is satisfactory even if the resistance does not lie wholly in the gas phase. The coefficient k_G on this basis is not an accurate value for the gas-film coefficient, although is proportional to it. It follows that, if the equilibrium curve is straight, either the gas-film or the liquid-film coefficient may be used. This simplification is of considerable value.

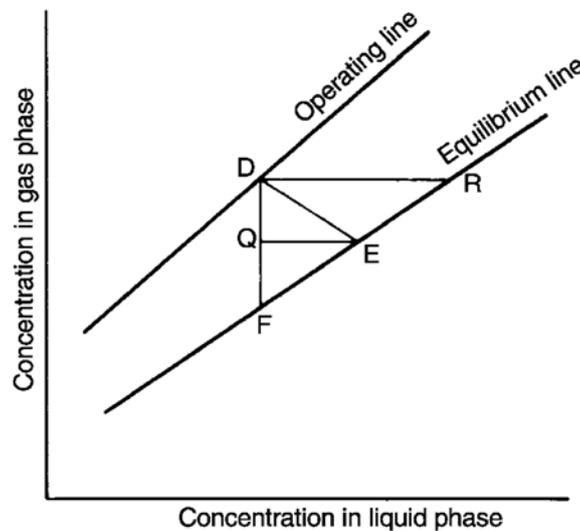


Figure 12.20. Driving force when equilibrium curve is a straight line

