CHAPTER 9

CONTACT EQUILIBRIUM PROCESSES

Biological raw materials are usually mixtures, and to prepare foods it may be necessary to separate some of the components of the mixtures.

One method, by which this separation can be carried out, is by the introduction of a *new phase* to the system and allowing the components of the original raw material to distribute themselves between the phases. For example, freshly dug vegetables have another phase, water, added to remove unwanted earth; a mixture of alcohol and water is heated to produce another phase, vapour, which is richer in alcohol than the mixture. By choosing the conditions, one phase is enriched whilst the other is depleted in some component or components. The maximum separation is reached at the equilibrium distribution of the components, but in practice separation may fall short of this as equilibrium is not attained. The components are distributed between the phases in accordance with *equilibrium distribution coefficients,* which give the relative concentrations in each phase when equilibrium has been reached. The two phases can then be separated by simple physical methods such as gravity settling. This process of contact, redistribution, and separation gives the name *contact equilibrium separations*. Successive stages can be used to enhance the separation.

An example is in the extraction of edible oil from soya beans. Beans containing oil are crushed, and then mixed with a solvent in which the oil, but not the other components of the beans, is soluble. Initially, the oil will be distributed between the beans and the solvent, but after efficient crushing and mixing the oil will be dissolved in the solvent. In the separation, some solvent and oil will be retained by the mass of beans; these will constitute one stream and the bulk of the solvent and oil the other. This process of contacting the two streams, of crushed beans and solvent, makes up one contact stage. To extract more oil from the beans, further contact stages can be provided by mixing the extracted beans with a fresh stream of solvent.

For economy and convenience, the solvent and oil stream from another extraction is often used instead of fresh solvent. So two streams, one containing beans and the other starting off as pure solvent, can move counter current to each other through a series of contact stages with progressive contacting followed by draining. In each stage of the process in which the streams come into contact, the material being transferred is distributed in equilibrium between the two streams. By removing the streams from the contact stage and contacting each with material of different composition, new equilibrium conditions are established and so separation can proceed.

In order to effect the desired separation of oil from beans, the process itself has introduced a further separation problem - the separation of the oil from the solvent. However, the solvent is chosen so that this subsequent separation is simple, for example by distillation. In some cases, such as washing, further separation of dissolved material from wash water may not be necessary and one stream may be rejected as waste. In other cases, such as distillation, the two streams are generated from the mixture of original components by vaporization of part of the mixture.

The two features that are common to all equilibrium contact processes are the attainment of, or approach to, equilibrium and the provision of contact stages. Equilibrium is reached when a component is so distributed between the two streams that there is no tendency for its concentration in either stream to change. Attainment of equilibrium may take appreciable time, and only if this time is available will effective equilibrium be reached. The opportunity to reach equilibrium is provided in each stage, and so with one or more stages the concentration of the transferred component changes progressively from one stream to the other, providing the desired separation.

Some examples of contact equilibrium separation processes are:
- Gas absorption
- Extraction and washing
- Crystallization
- Membrane separations
- Distillation

In addition, drying and humidification, and evaporation can be considered under this general heading for some purposes, but it seemed more appropriate in this book to take them separately.

For the analysis of these processes, there are two major sets of quantitative relationships; the equilibrium conditions that determine how the components are distributed between the phases, and the material flow balances that follow the progression of the components stage by stage.

PART 1. THEORY

CONCENTRATIONS

The driving force, which produces equilibrium distributions, is considered to be proportional at any time to the difference between the actual concentration and equilibrium concentration of the component being separated.. Thus, concentrations in contact equilibrium separation processes are linked with the general driving force concept.

Consider a case in which initially all of the molecules of some component *A* of a gas mixture are confined by a partition in one region of a system. The partition is then removed. Random movement among the gas molecules will, in time, distribute component *A* through the mixture. The greater the concentration of *A* in the partitioned region, the more rapidly will diffusion occur across the boundary once the partition is removed.

The relative proportions of the components in a mixture or a solution are expressed in terms of the concentrations. Any convenient units may be used for concentration, such as gg^{-1},gkg^{-1}, μgg^{-1}, percentages, parts per million, and so on.

Because the gas laws are based on numbers of molecules, it is often convenient to express concentrations in terms of the relative numbers of molecules of the components. The unit in this case is called the molecular fraction, shortened to mole fraction, which has been introduced in Chapter 2. The mole fraction of a component in a mixture is the proportion of the number of molecules of the component present to the total number of the molecules of all the components.

In a mixture which contains w_A kg of component A of molecular weight M_A and w_B kg of component B of molecular weight M_B, the mole fraction:

$$x_A = \frac{\text{number of moles of A}}{\text{number of moles of A + number of moles of B}}$$

$$x_A = (w_A /M_A) / (w_A /M_A + w_B /M_B) \qquad (9.1)$$

$$x_B = (w_B /M_B) / (w_A /M_A + w_B/M_B) \qquad (9.2)$$

Notice that $(x_A + x_B) = 1$, and so, $x_B = (1 - x_A)$

The definition of the mole fraction can be extended to any number of components in a multi-component mixture. The mole fraction of any one component again expresses the relative number of molecules of that component, to the total number of molecules of all the components in the mixture. Exactly the same method is followed if the weights of the components are expressed in grams. The mole fraction is a ratio, and so has no dimensions.

EXAMPLE 9.1. Mole fractions of ethanol in water

A solution of ethanol in water contains 30% of ethanol by weight. Calculate the mole fractions of ethanol and water in the solution.

Molecular weight of ethanol, C_2H_5OH, is 46 and the molecular weight of water, H_2O, is 18.
Since, in 100 kg of the mixture there are 30 kg of ethanol and 70 kg of water,

mole fraction of ethanol = (30/46)/ (30/46 + 70/18)
= 0.144
mole fraction of water = (70/18)/ (30/46 + 70/18)
= 0.856
= (1 - 0.144)

Concentrations of the components in gas mixtures can be expressed as weight fractions, mole fractions, and so on. When expressed as mole fractions, they can be related to the partial pressure of the components. The partial pressure of a component is that pressure which the component would exert if it alone occupied the whole volume of the mixture. Partial pressures of the components are additive, and their sum is equal to the total pressure of the mixture. The partial pressures and the mole fractions are proportional, so that the total pressure is made up from the sum of all the partial pressures, which are in the ratios of the mole fractions of the components.

If a gas mixture exists under a total pressure P and the mixture comprises a mole fraction x_A of component A, a mole fraction x_B of component B, a mole fraction x_C of component C and so on, then

$$P = Px_A + Px_B + Px_C + \ldots$$
$$= p_A + p_B + p_C + \ldots \qquad (9.3)$$

where p_A, p_B, p_C, are the partial pressures of components A, B, C...

In the case of gas mixtures, it is also possible to relate weight and volume proportions, as Avogadro's Law states that under equal conditions of temperature and pressure, equal volumes of gases contain equal numbers of molecules. This can be put in another way by saying that in a gas mixture, volume fractions will be proportional to mole fractions.

EXAMPLE 9.2. Mole fractions in air
Air is reported to contain 79 parts of nitrogen to 21 parts of oxygen, by volume. Calculate the mole fraction of oxygen and of nitrogen in the mixture and also the weight fractions and the mean molecular weight. Molecular weight of nitrogen is 28, and of oxygen 32.

Since mole fractions are proportional to volume fractions,

mole fraction of nitrogen = 79/(79 + 21)
= 0.79
mole fraction of oxygen = 21/(79 + 21)
= 0.21

The molecular weight of nitrogen, N_2, is 28 and of oxygen, O_2, is 32.

The weight fraction of nitrogen is given by:
weight of nitrogen/ (weight of nitrogen + weight of oxygen)= (79 x 28)/(79 x 28 + 21 x 32)
= 0.77

Similarly the weight fraction of oxygen = (21 x 32)/ (79 x 28 + 21 x 32)
= 0.23.

As the sum of the two weight fractions must add to 1, the weight fraction of the oxygen could have been found by the subtraction of (1 - 0.77) = 0.23.

To find the mean molecular weight, we must find the weight of one mole of the gas:

0.79 moles of N_2 weighing 0.79 x 28 kg = 22.1 kg
plus 0.21 moles of O_2 weighing 0.21 x 32kg = 6.7 kg
make up 1 mole of air weighing = 28.8 kg and so

Mean molecular weight of air is 28.8, say 29.

GAS/LIQUID EQUILIBRIA

Molecules of the components in a liquid mixture or a solution have a tendency to escape from the liquid surface into the gas above the solution. The escaping tendency sets up a pressure above the surface of the liquid, owing to the resultant concentration of the escaped molecules. This pressure is called the vapour pressure of the liquid.

The magnitude of the vapour pressure depends upon the liquid composition and upon the temperature. For pure liquids, vapour/pressure relationships have been tabulated and may be found in reference works such as Perry (1997) or the International Critical Tables. For a solution or a mixture, the various components in the liquid each exert their own partial vapour pressures.

When the liquid contains various components it has been found that, in many cases, the partial vapour pressure of any component is proportional to the mole fraction of that component in the liquid. That is,

$$p_A = H_A x_A \qquad (9.4)$$

where p_A is the partial vapour pressure of component A, H_A is a constant for component A at a given temperature and x_A is the mole fraction of component A in the liquid.

This relationship is approximately true for most systems and it is known as Henry's Law. The coefficient of proportionality H_A is known as the Henry's Law constant and has units of kPa mole fraction^{-1}. In reverse, Henry's Law can be used to predict the solubility of a gas in a liquid. If a gas exerts a given partial pressure above a liquid, then it will dissolve in the liquid until Henry's Law is satisfied and the mole fraction of the dissolved gas in the liquid is equal to the value appropriate to the partial pressure of that gas above the liquid. The reverse prediction can be useful for predicting the gas solubility in equilibrium below imposed gaseous atmospheres of various compositions and pressures.

EXAMPLE 9.3. Solubility of carbon dioxide in water

Given that the Henry's Law constant for carbon dioxide in water at 25°C is 1.6×10^5kPa mole fraction^{-1}, calculate the percentage solubility by weight of carbon dioxide in water under these conditions and at a partial pressure of carbon dioxide of 200kPa above the water.

From Henry's Law

$$\begin{aligned} p &= H x \\ 200 &= 1.6 \times 10^5 x \\ x &= 0.00125 \\ &= 1.25 \times 10^{-3} \\ &= (\underline{w_{CO2}}/44)/(\underline{w_{H20}}/18 + \underline{w_{CO2}}/44) \end{aligned}$$

But since (w_{H20}/18) » (w_{CO2}/44)

$$1.25 \times 10^{-3} \approx (w_{CO2}/44) / (w_{H20}/18)$$

and so

$$\begin{aligned} (w_{CO2}/ w_{H20}) &\approx 1.25 \times 10^{-3} / (44/18) \\ &= 3.1 \times 10^{-3} \\ &= 3.1 \times 10^{-1}\,\% \\ &= \underline{0.31\%} \end{aligned}$$

SOLID/LIQUID EQUILIBRIA

Liquids have a capacity to dissolve solids up to an extent, which is determined by the solubility of the particular solid material in that liquid. Solubility is a function of temperature and, in most cases, solubility increases with rising temperature. A solubility curve can be drawn to show this relationship, based on the equilibrium concentration in solution measured in convenient units, for example kg100kg^{-1} water as a function of temperature. Such a curve is illustrated in Fig. 9.1 for sodium nitrite in water.

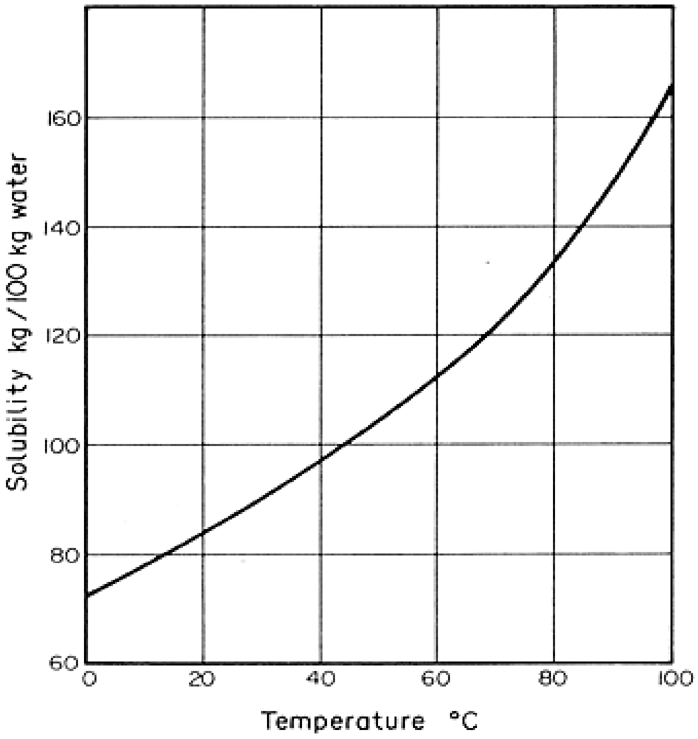


Figure 9.1 Solubility of sodium nitrite in water

There are some relatively rare systems in which solubility decreases with temperature, and they provide what is termed a reversed solubility curve.

The equilibrium solution, which is ultimately reached between solute and solvent, is called a saturated solution, implying that no further solute can be taken into solution at that particular temperature. An unsaturated solution plus solid solute is not in equilibrium, as the solvent can dissolve more of the solid. When a saturated solution is heated, if it has a normal solubility curve the solution then has a capacity to take up further solute material, and so it becomes unsaturated. Conversely, when a saturated solution is cooled it becomes supersaturated, and at equilibrium that solute which is in excess of the solubility level at the particular temperature will come out of solution, normally as crystals. However, this may not occur quickly and in the interim the solution is spoken of as supersaturated and it is said to be in a metastable state.

EQUILIBRIUM / CONCENTRATION RELATIONSHIPS

A contact equilibrium separation process is designed to reduce the concentration of a component in one phase, or flowing stream in a continuous process, and increase it in another. Conventionally, and just to distinguish one stream from another, one is called the overflow and the other the underflow. The terms referred originally to a system of two immiscible liquids, one lighter (the overflow) and the other heavier (the underflow) than the other, and between which the particular component was transferred. When there are several stages, the overflow and underflow streams then move off in opposite directions in a counter flow system.

Following standard chemical engineering nomenclature, the concentration of the component of interest in the lighter stream, that is the stream with the lower density, is denoted by y. For example, in a gas absorption system, the light stream would be the gas; in a distillation column, it would be the vapour stream; in a liquid extraction system, it would be the liquid overflow. The concentration of the component in the heavier stream is denoted by x. Thus we have two streams; in one the concentration of the component is y and in the other, the heavier stream, it is x. For a given system, it is often convenient to plot corresponding (equilibrium) values of y against x in an equilibrium diagram.

In the simple case of multistage oil extraction with a solvent, equilibrium is generally attained in each stage. The concentration of the oil is the same in the liquid solution spilling over or draining off in the overflow as it is in the liquid in the underflow containing the solids, so that in this case $y = x$ and the equilibrium/concentration diagram is a straight line.

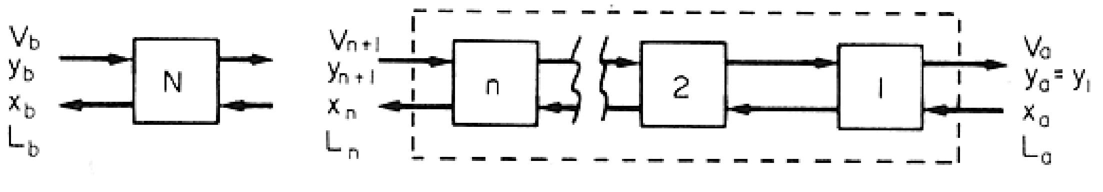
In gas absorption, such relationships as Henry's Law relate the concentration in the light gas phase to that in the heavy liquid phase and so enable the equilibrium diagram to be plotted. In crystallization, the equilibrium concentration corresponds to the solubility of the solute at the particular temperature. Across a membrane, there is some equilibrium distribution of the particular component of interest.

If the concentration in one stream is known, the equilibrium diagram allows us to read off the corresponding concentration in the other stream if equilibrium has been attained. The attainment of equilibrium takes time and this has to be taken into account when considering contact stages. The usual type of rate equation applies, in which the rate is given by the driving force divided by a resistance term. The driving force is the extent of the departure from equilibrium and generally is measured by concentration differences. Resistances have been classified in different ways but they are generally assumed to be concentrated at the phase boundary.

Stage contact systems in which equilibrium has not been attained are beyond the scope of this book. In many practical cases, allowance can be made for non-attained equilibrium by assuming an efficiency for each stage, in effect a percentage of equilibrium actually attained.

OPERATING CONDITIONS

In a series of contact stages, in which the components counter flow from one stage to another, mass balances can be written around any stage, or any number of stages. This enables operating equations to be set down to connect the flow rates and the compositions of the streams. Consider the generalized system shown in Fig. 9.2, in which there is a stage contact process operating with a number of stages and two contacting streams.



(a) (b)

Figure 9.2 Contact equilibrium stages

In Fig. 9.2(a), the mass flow of the light stream is denoted by V and the flow of the heavy stream by L and the concentration in the light phase by y and in the heavy phase by x.

Taking a balance over the first n stages as in Fig. 9.2(b), we can write, for the total flow, mass entering must equal mass leaving, so:

$$V_{n+1} + L_a = V_a + L_n$$

and for the component being exchanged:

$$V_{n+1}y_{n+1} + L_a x_a = V_a y_a + L_n x_n$$

where V is the mass flow rate of the light stream, L is the flow rate of the heavy stream, y is the concentration of the component being exchanged in the light stream and x is the concentration of the component being exchanged in the heavy stream. In the case of the subscripts, n denotes conditions at equilibrium in the nth stage, $(n + 1)$ denotes conditions at equilibrium in the $(n + 1)$th stage and a denotes the conditions of the streams entering and leaving stage 1, one being raw material and one product from that stage

Eliminating V_{n+1} between these equations, we have:

$$V_{n+1} = L_n - L_a + V_a$$

and so,

$$(L_n - L_a + V_a)\, y_{n+1} = V_a y_a + L_n x_n - L_a x_a$$

$$y_{n+1} = (V_a y_a + L_n x_n - L_a x_a)/(L_n - L_a + V_a)$$

$$y_{n+1} = x_n\,[L_n / (L_n - L_a + V_a)] + [(V_a y_a - L_a x_a)/ (L_n - L_a + V_a)] \quad (9.5)$$

This is an important equation as it expresses the concentration in one stream (the lighter stream) in the (n + 1)th stage in terms of the concentration in the other (heavier)stream in the nth stage.

In many practical cases in which equal quantities, or equal molal quantities, of the carrying streams move from one stage to another, that is where the flow rates are the same in all contact stages, then for:

heavier phase $L_{n+1} = L_n = ... L_a = L$
lighter phase $V_{n+1} = V_n = ... V_a. = V$

A simplified equation can be written for such cases:

$$y_{n+1} = x_n L / V + y_a - x_a L / V \qquad (9.6)$$

CALCULATION OF SEPARATION IN CONTACT EQUILIBRIUM PROCESSES

The separation, which will be effected in a given series of contact stages, can be calculated by combining the *equilibrium and the operating relationships*.

Starting at one end of the process, the terminal separation can be calculated from the given set of conditions. Knowing, say, the x value in the first stage, x_1, the equilibrium condition gives the corresponding value of y in this stage, y_1 Then eqn. (9.5) or eqn. (9.6) can be used to obtain y_2 then the equilibrium conditions give the corresponding x_2, and so on ...

EXAMPLE 9.4. Single stage steam stripping, of taints from cream
A continuous deodorizing system, involving a single stage steam stripping operation, is under consideration for the removal of taints from cream. If the taint component is present in the cream to the extent of 8 parts per million (ppm) and if steam is to be passed through the contact stage in the proportions of 0.75kg steam to every 1kg cream, calculate the concentration of the taint in the leaving cream. The equilibrium concentration distribution of the taint has been found experimentally to be in the ratio of 1 in the cream to 10 in the steam and it is assumed that equilibrium is reached in each stage.

Call the concentration of the taint in the cream x, and in the steam y, both as mass fractions,

From the condition that, at equilibrium, the concentration of the taint in the steam is 10 times that in the cream:

$$10x = y$$

and in particular, $10x_1 = y_1$

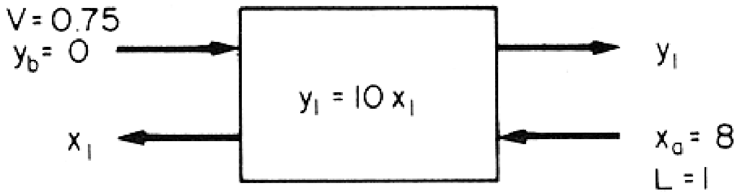
Now, y_1 the concentration of taint in the steam leaving the stage is also the concentration in the output steam:

$$y_1 = y_a = 10x_1$$

The incoming steam concentration = $y_2 = y_b = 0$ as there is no taint in the entering steam.
The taint concentration in the entering cream is x_a = 8ppm.

These are shown diagrammatically in Fig. 9.3.

Steam



Cream

Figure 9.3 Flows into and out from a stage

The problem is to determine x_1 the concentration of taint in the product cream.

Basis is 1kg of cream.
The mass ratio of stream flows is 1 of cream to 0.75 of steam and if no steam is condensed this ratio will be preserved through the stage.

1/0.75 = 1.33 is the ratio of cream flow rate to steam flow rate = L/V.

Applying eqn. (9.6) to the one stage n = 1,

$$y_2 \qquad = x_n L/V + y_a - x_a L/V$$

$$y_2 = 0 \qquad = x_1 1.33 + 10x_1 - 8 \times 1.33$$

$$x_1 \qquad = 10.64/11.33$$

$$= \underline{0.94\text{ppm}}$$

which is the concentration of the taint in the leaving cream, having been reduced from 8 ppm.

This simple example could have been solved directly without using the formula, but it shows the way in which the formula and the equilibrium conditions can be applied.

McCabe -Thiele plot

Based on the step-by-step method of calculation, it was suggested by McCabe and Thiele (1925) that the operating and equilibrium relationships could very conveniently be combined in a single graph called a McCabe -Thiele plot.

The essential feature of their method is that whereas the equilibrium line is plotted directly, x_n against y_n, the operating relationships are plotted as x_n against y_{n+1}. Inspection of eqn. (9.5) shows that it gives y_{n+1} in terms of x_n and the graph of this is called the operating line. In the special case of eqn. (9.6), the operating line is a straight line whose slope is L/V and whose intercept on the y-axis is ($y_a - x_a L/V$).

Considering any stage in the process, it might be for example the first stage, we have the value of y from given or overall conditions. Proceeding at constant y to the equilibrium line we can then read off the corresponding value of x, which is x_1. From x_1 we proceed at constant x across to the operating line at which the intercept gives the value of y_2. Then the process can be repeated for y_2 to x_2, then to y_3, and so on.

Drawing horizontal and vertical lines to show this, as in Fig. 9.4 in Example 9.5, a step pattern is traced out on the graph. Each step represents a stage in the process at which contact is provided between the streams, and the equilibrium attained. Proceeding step-by-step, it is simple to insert sufficient steps to move to a required final concentration in one of the streams and so to be able to count the number of stages of contact needed to obtain this required separation.

PART 2 APPLICATIONS

GAS ABSORPTION

Gas absorption/desorption is a process in which a gaseous mixture is brought into contact with a liquid and during this contact a component is transferred between the gas stream and the liquid stream. The gas may be bubbled through the liquid, or it may pass over streams of the liquid, arranged to provide a large surface through which the mass transfer can occur. The liquid film in this latter case can flow down the sides of columns or over packing, or it can cascade from one tray to another with the liquid falling and the gas rising in the counter flow. The gas, or components of it, either dissolves in the liquid (absorption)or extracts a volatile component from the liquid (desorption).

An example of absorption is found in hydrogenation of oils, in which the hydrogen gas is bubbled through the oil with which it reacts. Generally, there is a catalyst present also to promote the reaction. The hydrogen is absorbed into the oil, reacting with the unsaturated bonds in the oil to harden it. Another example of gas absorption is in the carbonation of beverages. Carbon dioxide under pressure is dissolved in the liquid beverage, so that when the pressure is subsequently released on opening the container, effervescence occurs.

An example of desorption is found in the steam stripping of fats and oils in which steam is brought into contact with the liquid fat or oil, and undesired components of the fat or oil pass out with the steam. This is used in the deodorizing of natural oils before blending them into food products such as margarine, and in the stripping of unwanted flavours from cream before it is made into butter. The equilibrium conditions arise from the balance of concentrations of the gas or the volatile flavour, between the gas and the liquid streams.

In the gas absorption process, sufficient time must be allowed for equilibrium to be attained so that the greatest possible transfer can occur and, also, opportunity must be provided for contacts between the streams to occur under favourable conditions.

Rate of Gas Absorption

The rates of mass transfer in gas absorption are controlled by the extent of the departure of the system from the equilibrium concentrations and by the resistance offered to the mass transfer by the streams of liquid and gas. Thus, we have the familiar expression:

rate of absorption = driving force/resistance,

The driving force is the extent of the difference between the actual concentrations and the equilibrium concentrations. This is represented in terms of concentration differences.

For the resistance, the situation is complicated, but for practical purposes it is adequate to consider the whole of the resistance to be concentrated at the interface between the two streams. At the interface, two films are postulated, one in the liquid and one in the gas. The two-film theory of Lewis and Whitman defines these resistances separately, a gas film resistance and a liquid film resistance. They are treated very similarly to surface heat transfer coefficients and the resistances of the two films can be combined in an overall resistance similar to an overall heat transfer coefficient.

The driving forces through each of the films are considered to be the concentration differences between the material in the bulk liquid or gas and the material in the liquid or gas at the interface. In practice, it is seldom possible to measure interfacial conditions and overall coefficients are used giving the equation

$$\mathrm{d}w/\mathrm{d}t = K_l A\,(x^* - x) = K_g A(y - y^*) \qquad (9.7)$$

where $\mathrm{d}w/\mathrm{d}t$ is the quantity of gas passing across the interface in unit time, K_l is the overall liquid mass transfer coefficient, K_g is the overall gas mass transfer coefficient, A is the interfacial area and x, y are the concentrations of the gas being transferred, in the liquid and gas streams respectively. The quantities of x^* and y^* are introduced into the equation because it is usual to express concentrations in the liquid and in the gas in different units. With these, x^* represents the concentration in the liquid which would be in equilibrium with a concentration y in the gas and y^* the concentration in the gas stream which would be in equilibrium with a concentration x in the liquid.

Equation (9.7) can be integrated and used to calculate overall rates of gas absorption or desorption. For details of the procedure, reference should be made to works such as Perry (1997), Charm (1971), Coulson and Richardson (1978) or McCabe and Smith (1975).

Stage Equi1ibrium Gas Absorption

The performance of counter current, stage contact, gas absorption equipment can be calculated if the operating and equilibrium conditions are known. The liquid stream and the gas stream are brought into contact in each stage and it is assumed that sufficient time is allowed for equilibrium to be reached. In cases where sufficient time is not available for equilibration, the rate equations have to be introduced and this complicates the analysis. However, in many cases of practical importance in the food industry, either the time is sufficient to reach equilibrium, or else the calculation can be carried out on the assumption that it is and a stage efficiency term, a fractional attainment of equilibrium, introduced to allow for the conditions actually attained. Appropriate efficiency values can sometimes be found from published information, or sought experimentally.

After the streams in a contact stage have come to equilibrium, they are separated and then pass in opposite directions to the adjacent stages. The separation of the gas and the liquid does not generally present great difficulty and some form of cyclone separator is often used.

In order to calculate the equipment performance, operating conditions must be known or found from the mass balances. Very often the known factors are:

- gas and liquid rates of flow,
- inlet conditions of gas and liquid,
- one of the outlet conditions, and
- equilibrium relationships.

The processing problem is to find how many contact stages are necessary to achieve the concentration change that is required. An overall mass balance will give the remaining outlet condition and then the operating line can be drawn. The equilibrium line is then plotted on the same diagram, and the McCabe-Thiele construction applied to solve the problem.

EXAMPLE 9.5. Multiple stage steam stripping of taints from cream
In Example 9.4, a calculation was made for a single stage, steam stripping process to remove taints in the cream, by contact with a counter flow current of steam.
Consider, now, the case of a rather more difficult taint to remove in which the equilibrium concentration of the taint in the steam is only 7.5 times as great as that in the cream. If the relative flow rates of cream and steam are given in the ratio 1: 0.75, how many contact stages would be required to reduce the taint concentration in the cream to 0.3ppm assuming (a) 100% stage efficiency and (b) 70% stage efficiency? The initial concentration of the taint is 10ppm.

Mass balance

Inlet cream taint concentration = 10ppm
= x_a
Outlet cream taint concentration = 0.3ppm
= x_n
Inlet steam taint concentration = 0ppm
= y_{n+1}

Assume a cream flow rate L = 100 arbitrary units
so steam flow rate V = 75

If y_1 is the outlet steam taint concentration,
total taint into equipment = total taint out of equipment.

$$100(10) = 75y_1 + 100(0.3)$$

$$100(10 - 0.3) = 75y_1$$

Therefore $y_1 = 12.9\text{ppm} = y_a$

From eqn. (9.6)

$$Y_{n+1} = x_n L/V + y_a - x_a L/V$$

$$Y_{n+1} = x_n\,(100/75) + 12.9 - 10\,(100/75)$$
$$= 1.33\,x_n - 0.43$$

Equilibrium condition: $Y_n = 7.5x_n$

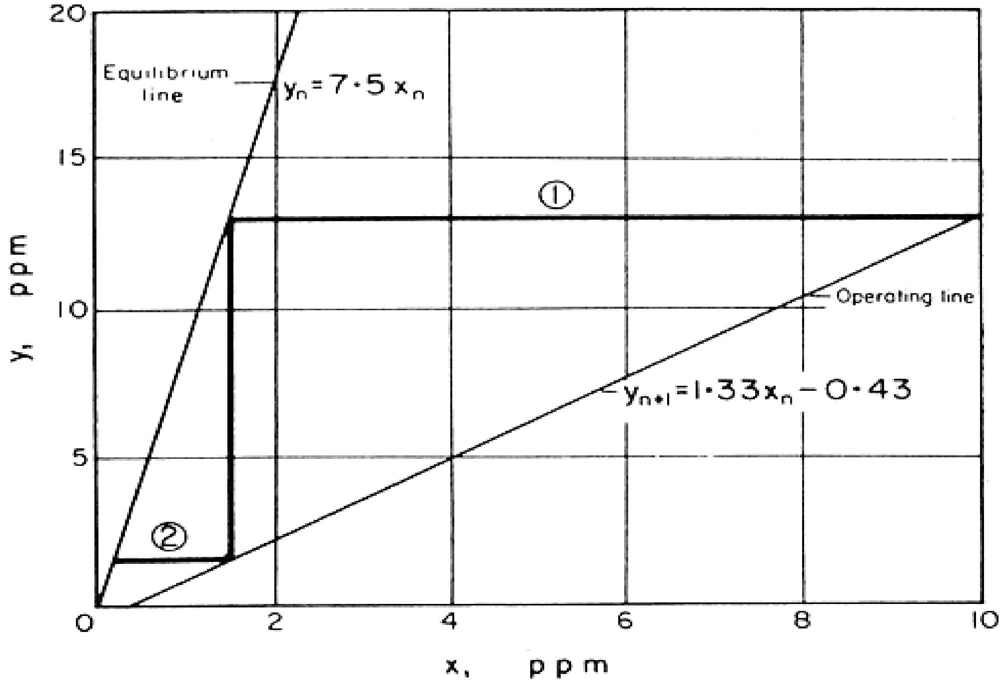


Figure 9.4 Steam stripping of cream: McCabe -Thiele plot

On the graph of Fig. 9.4 are shown the operating line, plotting x_n against y_{n+1}, and the equilibrium line in which x_n, is plotted against y_n. Starting from one terminal condition on the operating line, the stage contact steps are drawn in until the desired other terminal concentrations are reached. Each of the numbered horizontal lines represents one stage

From the operating and equilibrium plotted on Fig. 9.4, it can be seen that two contact stages are sufficient to effect the required separation. The construction assumes 100% efficiency so that, with a stage efficiency of 70%, the number of stages required would be 2(100/70) and this equals approximately three stages.

So the number of contact stages required assuming:

(a) 100% efficiency = 2, and
(b) 70% efficiency = 3.

Notice that only a small number of stages is required for this operation, as the equilibrium condition is quite well removed from unity and the steam flow is of the same order as that of the cream. A smaller equilibrium constant, or a smaller relative steam-flow rate, would increase the required number of contact stages.

Gas Absorption Equipment

Gas absorption equipment is designed to achieve the greatest practicable interfacial area between the gas and the liquid streams, so that liquid sprays and gas bubbling devices are often employed. In many cases, a vertical array of trays is so arranged that the liquid descends over a series of perforated trays, or flows down over ceramic packing that fills a tower.

For the hydrogenation of oils, absorption is followed by reaction of the hydrogen with the oil, and a nickel catalyst is used to speed up the reactions. Also, pressure is applied to increase gas concentrations and therefore speed up the reaction rates. Practical problems are concerned with arranging distribution of the catalyst, as well as of oil and hydrogen. Some designs spray oil and catalyst into hydrogen, others bubble hydrogen through a continuous oil phase in which catalyst particles are suspended.

For the stripping of volatile flavours and taints in deodorizing equipment, the steam phase is in general the continuous one and the liquid is sprayed into this and then separated. In one design of cream deodorizing plant, cream is sprayed into an atmosphere of steam and the two streams then pass on to the next stages, or the steam may be condensed and fresh steam used in the next stage.

EXTRACTION AND WASHING

It is often convenient to use a liquid in order to carry out a separation process. The liquid is thoroughly mixed with either solids or other liquid from which the component is to be removed and then the two streams are separated.

In the case of solids, the separation of the two streams is generally by simple gravity settling. Sometimes it is the solution in the introduced liquid that is the product required, such as in the extraction of coffee from coffee beans with water. In other cases, the washed solid may be the product as in the washing of butter. The term ‘washing’ is generally used where an unwanted constituent is removed in a stream of water. Extraction is also an essential stage in the sugar industry when soluble sucrose is removed by water extraction from sugar cane or sugar beet. Washing occurs so frequently as to need no specific examples.

To separate liquid streams, the liquids must be immiscible, such as oil and water. Liquid/liquid extraction is the name used when both streams in the extraction are liquid. Examples of extraction are found in the edible oil industry in which oil is extracted from natural products such as peanuts, soya beans, rape seeds, sunflower seeds and so on. Liquid/liquid extraction is used in the extraction of fatty acids.

Factors controlling the operation are:

- area of contact between the streams,
- time of contact,
- properties of the materials so far as the equilibrium distribution of the transferred component is concerned,
- number of contact stages employed.

In extraction from a solid, the solid matrix may hinder diffusion and so control the rate of extraction.

Rate of Extraction

The solution process can be considered in terms of the usual rate equation

rate of solution = driving force/resistance.

In this case, the driving force is the difference between the concentration of the component being transferred, the solute, at the solid interface and in the bulk of the solvent stream. For liquid/liquid extraction, a double film must be considered, at the interface and in the bulk of the other stream.

For solution from a solid component, the equation can be written:

$$\mathrm{d}w/\mathrm{d}t = K_l A(y_s - y) \qquad (9.8)$$

where $\mathrm{d}w/\mathrm{d}t$ is the rate of solution, K_l is the mass transfer coefficient, A is the interfacial area, and y_s and y, are the concentrations of the soluble component in the bulk of the liquid and at the interface. It is usually assumed that a saturated solution is formed at the interface and y_s is the concentration of a saturated solution at the temperature of the system.

Examination of eqn. (9.8) shows the effects of some of the factors, which can be used to speed up rates of solution. Fine divisions of the solid component increases the interfacial area A. Good mixing ensures that the local concentration is equal to the mean bulk concentration. In other words, it means that there are no local higher concentrations arising from bad stirring increasing the value of y and so cutting down the rate of solution. An increase in the temperature of the system will, in general, increase rates of solution by not only increasing K_l, which is related to diffusion, but also by increasing the solubility of the solute and so increasing y_s.

In the simple case of extraction from a solid in a contact stage, a mass balance on the solute gives the equation:

$$\mathrm{d}w = V\mathrm{d}y \qquad (9.9)$$

where V is the quantity of liquid in the liquid stream.

Substituting for $\mathrm{d}w$ in eqn. (9.8) we then have:

$$V\mathrm{d}y/\mathrm{d}t = K_l A(y_s - y)$$

which can then be integrated over time t during which time the concentration goes from an initial value of y_o to a concentration y, giving

$$\log_e [(y_s - y_o)/(y_s - y)] = tK_l A/V. \qquad (9.10)$$

Equation (9.10) shows, as might be expected, that the approach to equilibrium is exponential with time. The equation cannot often be applied because of the difficulty of knowing or measuring the interfacial area *A*. In practice, suitable extraction times are generally arrived at by experimentation under the particular conditions that are anticipated for the plant.

Stage Equilibrium Extraction

Analysis of an extraction operation depends upon establishing the equilibrium and operating conditions. The equilibrium conditions are, in general, simple. Considering the extraction of a solute from a solid matrix, it is assumed that the whole of the solute is dissolved in the liquid in one stage, which in effect accomplishes the desired separation. However, it is not possible then to separate all of the liquid from the solid because some solution is retained with the solid matrix and this solution contains solute. As the solid retains solution with it, the content of solute in this retained solution must be then progressively reduced by stage contacts. For example, in the extraction of oil from soya beans using hexane or other hydrocarbon solvents, the solid beans matrix may retain its own weight, or more, of the solution after settling. This retained solution may therefore contain a substantial proportion of the oil. The equilibrium conditions are simple because the concentration of the oil is the same in the external solution that can be separated as it is in the solution that remains with the seed matrix. Consequently, y, the concentration of oil in the "light" liquid stream, is equal to x, the concentration of oil in the solution in the "heavy" stream accompanying the seed matrix. The equilibrium line is, therefore, plotted from the relation $y = x$.

The operating conditions can be analysed by writing mass balances round the stages to give the eqn. (9.5). The plant is generally arranged in the form of a series of mixers, followed by settlers in which the two streams are separated prior to passing to the next stage of mixers. For most purposes of analysis, the solid matrix need not be considered; the solids can be thought of as just the means by which the two solution streams are separated after each stage. So long as the same quantity of solid material passes from stage to stage, and also the solids retain the same quantity of liquid after each settling operation, the analysis is straightforward. In eqn. (9.5), V refers to the liquid overflow stream from the settlers, and L to the mixture of solid and solution that is settled out and passes on with the underflow.

If the underflow retains the same quantity of solution as it passes from stage to stage, eqn. (9.5) simplifies to eqn. (9.6). The extraction operation can then be analysed by application of step-by-step solution of the equations for each stage, or by the use of the McCabe-Thiele graphical method.

EXAMPLE 9.6. Counter current extraction of oil from soya beans with hexane
Oil is to be extracted from soya beans in a counter current, stage contact, extraction apparatus, using hexane. If the initial oil content of the beans is 18%, the final extract solution is to contain 40% of oil, and if 90% of the total oil is to be extracted, calculate the number of contact stages that are necessary. Assume that the oil is extracted from the beans in the first mixer, that equilibrium is reached in each stage, and that the crushed bean solids in the underflow retain in addition half their weight of solution after each settling stage.

The extraction plant is illustrated diagrammatically in Fig. 9.5.

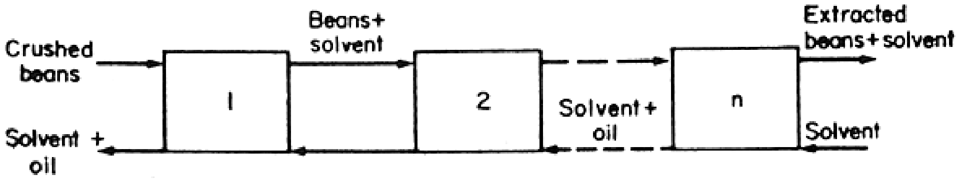


Figure 9.5 Hexane extraction of oil from soya beans in stages

Each box represents a mixing/settling stage and the stages are numbered from the stage at which the crushed beans enter.

The underflow will be constant from stage to stage (a constant proportion of solution is retained by the crushed beans) except for the first stage in which the entering crushed beans (bean matrix and oil) are accompanied by no solvent. After the first stage, the underflow is constant and so all stages but the first can be treated by the use of eqn. (9.6).

To illustrate the principles involved, the problem will be worked out from stage-by-stage mass balances, and using the McCabe-Thiele graphical method.

Basis for calculation: 100kg raw material (beans and their associated oil) entering stage 1. Concentrations of oil will be expressed as weight fractions.

Overall mass balance
In 100kg raw material there will be 18% oil, that is 82kg bean solids and 18kg oil. In the final underflow, 82 kg bean solids will retain 41 kg of solution, the solution will contain 10% of the initial oil in the beans, that is, 1.8kg so that there will be (18 - 1.8) = 16.2kg of oil in the final overflow,

Extract contains (16.2 x 60/40) = 24.3kg of solvent
Total volume of final overflow = 16.2 + 24.3 = 40.5kg
Total solvent entering = (39.2 + 24.3) = 63.5kg

Note that the solution passing as overflow between the stages is the same weight as the solvent entering the whole system, i.e. 63.5kg.

MASS BALANCE

Basis: 100kg beans

Mass in (kg)			**Mass out (kg)**		
Underflow			*Underflow*		
Raw beans		100.0	Extracted beans + solution		123.0
Bean solids	82.0		Bean solids	82.0	
Oil	18.0		Oil	1.8	
			Solvent	39.2	
Overflow			*Overflow*		
Solvent		63.5	Total extract		40.5
			Solvent	24.3	
			Oil	16.2	
Total		163.5	Total		163.5

Analysis of stage 1

Oil concentration in underflow = product concentration = 0.4.
It is an equilibrium stage, so oil concentration in underflow equals oil concentration in overflow. Let y_2 represent the concentration of oil in the overflow from stage 2 passing in to stage 1. Then oil entering stage 1 equals oil leaving stage 1.
Therefore balance on oil:

$$63.5y_2 + 18 = 41 \times 0.4 + 40.5 \times 0.4$$
$$y_2 = 0.23.$$

Analysis of stage 2

$$x_2 = y_2 = 0.23$$

Therefore balance on oil:

$$41 \times 0.4 + 63.5y_3 = 63.5 \times 0.23 + 41 \times 0.23$$
$$y_3 = 0.12.$$

Analysis of stage 3

$$x_3 = y_3 = 0.12$$

Therefore balance on oil:

$$41 \times 0.23 + 63.5y_4 = 63.5 \times 0.12 + 41 \times 0.12$$
$$y_4 = 0.049$$

Analysis of stage 4

$$x_4 = y_4 = 0.049,$$

Therefore balance on oil

$$41 \times 0.12 + 63.5\, y_5 = 63.5 \times 0.049 + 41 \times 0.049,$$
$$y_5 = 0.00315.$$

The required terminal condition is that the underflow from the final nth stage will have less than 1.8 kg of oil, that is, that x_n is less than 1.8/41 = 0.044.

Since $x_n = y_n$ and we have calculated that y_5 is 0.00315 which is less than 0.044 (whereas $y_4 = 0.049$ was not), four stages of contact will be sufficient for the requirements of the process.

Using the graphical method, the general eqn. (9.6) can be applied to all stages after the first. From the calculations above for the first stage, we have $x_1 = 0.4$, $y_2 = 0.23$ and these can be considered as the entry conditions x_a and y_a for the series of subsequent stages.

Applying eqn. (9.6):

$$y_{n+1} = x_n L/V + y_a - x_a L/V$$

Now $L = 41$ $V = 63.5$ $y_a = 0.23$ $x_a = 0.4$

Therefore the operating line equation is:

$$y_{n+1} = 0.646\, x_n - 0.028$$

The equilibrium line is:

$$y_n = x_n$$

The operating line and the equilibrium line have been plotted on Fig. 9.6.

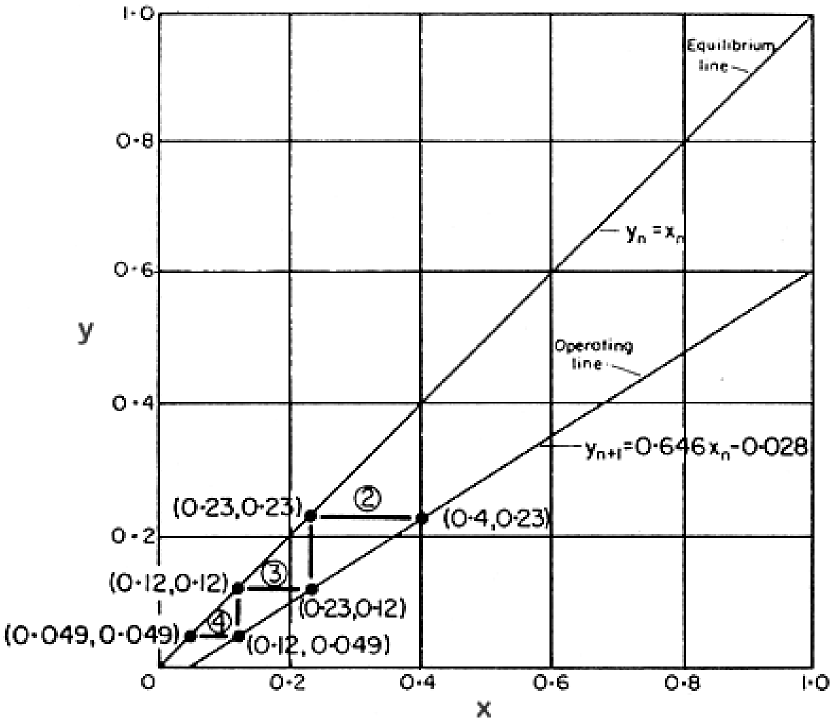


Figure 9.6 Hexane extraction of oil from soyabeans: McCabe - Thiele plot

The McCabe -Thiele construction has been applied, starting with the entry conditions to stage 2 (stage 1 being the initial mixing stage) on the operating line, and it can be seen that three steps are not sufficient, but that four steps give more than the minimum separation required. Since the initial stage is included but not shown on the diagram, four stages are necessary, which is the same result as was obtained from the step-by-step calculations.

The step construction on the McCabe -Thiele diagram can also be started from the *n*th stage, since we know that y_{n+1} which is the entering fresh solvent, equals 0. This will also give the same number of stages, but it will apparently show slightly different stage concentrations. The apparent discrepancy arises from the fact that in the overall balance, a final (given) concentration of oil in the overflow stream of 0.044 was used, and both the step-by-step equations and the McCabe-Thiele operating line depend upon this. In fact, this concentration can never be reached using a whole number of steps under the conditions of the problem and to refine the calculation it would be necessary to use trial-and-error methods. However, the above method is a sufficiently close approximation for most purposes.

In some practical extraction applications, the solids may retain different quantities of the solvent in some stages of the plant. For example, this might be due to rising concentrations of extract having higher viscosities. In this case, the operating line is not straight, but step-by-step methods can still be used. For some of the more complex situations other graphical methods using triangular diagrams can be employed and a discussion of their use may be found in Charm (1980), Coulson and Richardson (1978) or Treybal (1980).

It should be noted that in the chemical engineering literature what has here been called extraction is more often called leaching, the term extraction being reserved for liquid/liquid contacting using immiscible liquids. "Extraction" is, however, in quite general use in the food industry to describe processes such as the one in the above example, whereas the term "leaching" would probably only cause confusion.

Washing

Washing is almost identical to extraction, the main distinction being one of emphasis; in washing the inert material is the required product, and the solvent used is water which is cheap and readily available. Various washing situations are encountered and can be analysed. That to be considered is one in which a solid precipitate, the product, retains water which also contains residues of the mother liquor so that on drying without washing these residues will remain with the product. The washing is designed to remove them, and examples are butter, casein and cheese washing in the dairy industry.

Calculations on counter current washing can be carried out using the same methods as discussed under extraction, working from the operating and equilibrium conditions. In washing, fresh water is often used for each stage and the calculations for this are also straightforward.

In multiple washing, the water content of the material is x_w (weight fraction) and a fraction of this, x, is impurity, and to this is added yx_w of wash water, and after washing thoroughly, the material is allowed to drain. After draining it retains the same quantity, approximately, of water as before, x_w. The residual yx_w of wash liquid, now at equilibrium containing the same concentration of impurities as in the liquid remaining with the solid, runs to waste. Of course in situations in which water is scarce, counter current washing may be worthwhile.

The impurity which was formerly contained in x_w of water is now in a mass ($x_w + yx_w$); its concentration x has fallen by the ratio of these volumes, that is to $x\,[x_w/(x_w + yx_w)]$.

So the concentration, remaining with the solid, x_1 is given by:

after one washing:

$$x_1 = x[x_w / x_w(1 + y)] = x[1/(1 + y)]$$

after two washings:

$$x_2 = x_1[1/(1 + y)] = x[1/(1 + y)]^2$$

and so after n washings:

$$x_n = x[1/(1 + y)]^n \qquad (9.11)$$

If, on the other hand, the material is washed with the same total quantity of water as in the n washing stages, that is nyx_w, but all in one stage, the impurity content will be:

$$x_n' = x[1/(1 + ny)] \qquad (9.12)$$

and it is clear that the multiple contact washing is very much more efficient in reducing the impurity content than is single contact washing, both using the same total quantity of water.

EXAMPLE 9.7. Washing of casein curd

After precipitation and draining procedures, it is found that 100kg of fresh casein curd has a liquid content of 66% and this liquid contains 4.5% of lactose. The curd is washed three times with 194kg of fresh water each time. Calculate the residual lactose in the casein after drying. Also calculate the quantity of water that would have to be used in a single wash to attain the same lactose content in the curd as obtained after three washings. Assume perfect washing, and draining of curd to 66% of moisture each time.

100kg of curd contain 66kg solution. The 66kg of solution contain 4.5% that is 3 kg of lactose.

In the first wash (194 + 66) = 260kg of solution contain 3kg lactose.
In 66 kg of solution lactose remaining there will be (66/260) x 3 = 0.76kg .
After the second wash the lactose remaining will be (66/260) x 0.76 = 0.19kg
After the third wash the lactose remaining will be (66/260) x 0.19 = 0.048kg

Or, after three washings lactose remaining will be 3 x $(66/260)^3$ = 0.048kg
(Similar to the stage analysis.)

So, after washing and drying 0.048kg of lactose will remain with 34kg dry casein so that

lactose content of the product = 0.048/34.05
= 0.14%
and total wash water = 3 x 194 = 582kg

To reduce the impurity content to 0.048 kg in one wash would require *x* kg of water, where

$$(3 \times 66)/(x + 66) = 0.048\text{kg}$$
$$x = 4060\text{kg}$$

and so the total wash water = 4060kg

Alternatively using eqns. (9.11) and (9.12)

$$x_n' = x[1/(1 + y)]$$
$$= 3[1/(1 + 194/66)]^3$$
$$= 0.049$$

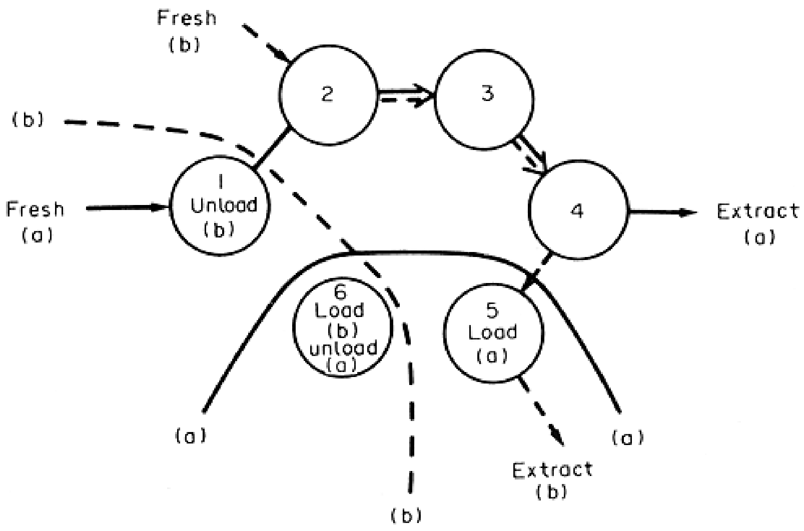
$$x_n' = x[1/(ny + 1)]$$
$$0.049 = 3[1/(ny + 1)]$$
$$ny = 61.5.$$

Total wash water = $ny x_w$ = 61.5 x 66
= 4060kg.

Extraction and Washing Equipment

The first stage in an extraction process is generally mechanical grinding, in which the raw material is shredded, ground or pressed into suitably small pieces or flakes to give a large contact area for the extraction. In some instances, for example in sugar cane processing and in the extraction of vegetable oils, a substantial proportion of the desired products can be removed directly by expression at this stage and then the remaining solids are passed to the extraction plant. Fluid solvents are easy to pump and so overflows are often easier to handle than underflows and sometimes the solids may be left and solvent from successive stages brought to them.

This is the case in the conventional extraction battery. In this a number of tanks, each suitable both for mixing and for settling, are arranged in a row or a ring. The solids remain in the one mixer/settler and the solvent is moved progressively round the ring of tanks, the number, n, often being about 12. At any time, two of the tanks are out of operation, one being emptied and the other being filled. In the remaining (n - 2) tanks, extraction is proceeding with the extracting liquid solvent, usually water, being passed through the tanks in sequence, the "oldest" (most highly extracted) tank receiving the fresh liquid and the "youngest" (newly filled with fresh raw material) tank receiving the most concentrated liquid. After leaving this "youngest" tank, the concentrated liquid passes from the extraction battery to the next stage of the process. After a suitable interval, the connections are altered so that the tank which has just been filled becomes the new “youngest" tank. The former "oldest" tank comes out of the sequence and is emptied, the one that was being emptied is filled and the remaining tanks retain their sequence but with each becoming one stage "older". This procedure which is illustrated in Fig. 9.7 in effect accomplishes counter current extraction, but with only the liquid physically having to be moved apart from the emptying and filling in the terminal tanks.



Phase (a) Cells 5,6 out ; 5 loading, 6 unloading
1 . . . 4 extracting

Phase (b) Cells 6, 1 out ; 6 loading, 1 unloading
2 . . . 5 extracting

Thence to phase (c), (d) . . . . . etc.

Figure 9.7 Extraction battery

In the same way and for the same reasons as with counter flow heat exchangers, this counter current (or counter flow) extraction system provides the maximum mean driving force, the log mean concentration difference in this case, contrasting with the log mean temperature difference in the heat exchanger. This ensures that the equipment is used efficiently.

In some other extractors, the solids are placed in a vertical bucket conveyor and moved up through a tower down which a stream of solvent flows. Other forms of conveyor may also be used, such as screws or metal bands, to move the solids against the solvent flow. Sometimes centrifugal forces are used for conveying, or for separating after contacting.

Washing is generally carried out in equipment that allows flushing of fresh water over the material to be washed. In some cases, the washing is carried out in a series of stages. Although water is cheap, in many cases very large quantities are used for washing so that attention paid to more efficient washing methods may well be worthwhile. Much mechanical ingenuity has been expended upon equipment for washing and many types of washers are described in the literature.

CRYSTALLIZATION

Crystallization is an example of a separation process in which mass is transferred from a liquid solution, whose composition is generally mixed, to a pure solid crystal. Soluble components are removed from solution by adjusting the conditions so that the solution becomes supersaturated and excess solute crystallizes out in a pure form. This is generally accomplished by lowering the temperature, or by concentration of the solution, in each case to form a supersaturated solution from which crystallization can occur. The equilibrium is established between the crystals and the surrounding solution, the mother liquor. The manufacture of sucrose, from sugar cane or sugar beet, is an important example of crystallization in food technology. Crystallization is also used in the manufacture of other sugars, such as glucose and lactose, in the manufacture of food additives, such as salt, and in the processing of foodstuffs, such as ice cream. In the manufacture of sucrose from cane, the juice is expressed, water is added to the solid waste and the sugar is pressed out from the residual cane as a solution. This solution is purified and then concentrated to allow the sucrose to crystallize out from the solution.

Crystallization Equilibrium

Once crystallization is concluded, equilibrium is set up between the crystals of pure solute and the residual mother liquor, the balance being determined by the solubility (concentration) and the temperature. The driving force making the crystals grow is the concentration excess (supersaturation) of the solution above the equilibrium (saturation) level. The resistances to growth are the resistance to mass transfer within the solution and the energy needed at the crystal surface for incoming molecules to orient themselves to the crystal lattice.

Solubility and Saturation

Solubility is defined as the maximum weight of anhydrous solute that will dissolve in 100 g of solvent. In the food industry, the solvent is generally water.

Solubility is a function of temperature. For most food materials increase in temperature increases the solubility of the solute as shown for sucrose in Fig. 9.8. Pressure has very little effect on solubility.

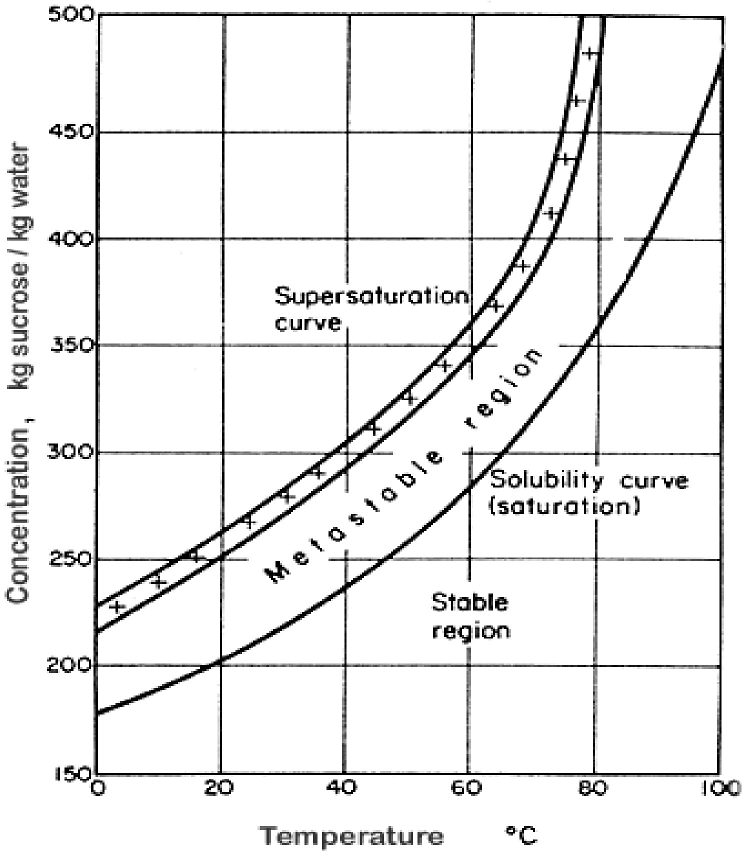


Figure 9.8 Solubility and saturation curves for sucrose in water

During crystallization, the crystals are grown from solutions with concentrations higher than the saturation level in the solubility curves. Above the supersaturation line, crystals form spontaneously and rapidly, without external initiating action. This is called spontaneous nucleation. In the area of concentrations between the saturation and the supersaturation curves, the metastable region, the rate of initiation of crystallization is slow; aggregates of molecules form but then disperse again and they will not grow unless seed crystals are added. Seed crystals are small crystals, generally of the solute, which then grow by deposition on them of further solute from the solution. This growth continues until the solution concentration falls to the saturation line. Below the saturation curve there is no crystal growth, crystals instead dissolve.

EXAMPLE 9.8. Crystallization of sodium chloride

If sodium chloride solution, at a temperature of 40°C, has a concentration of 50% when the solubility of sodium chloride at this temperature is 36.6g/100 g water, calculate the quantity of sodium chloride crystals that will form once crystallization has started.

Weight of salt in solution = 50g/100 g solution
= 50g/50g water

= 100g/100g water.

Saturation concentration = 36.6g/100g water

Weight crystallized out = (100 - 36.6)g/l00g water

= 63.4g/100g water

To remove more salt, this solution would have to be concentrated by removal of water, or else cooled to a lower temperature.

Heat of crystallization

When a solution is cooled to produce a supersaturated solution and hence to cause crystallization, the heat that must be removed is the sum of the sensible heat necessary to cool the solution and the heat of crystallization. When using evaporation to achieve the supersaturation, the heat of vaporization must also be taken into account. Because few heats of crystallization are available, it is usual to take the heat of crystallization as equal to the heat of solution to form a saturated solution. Theoretically, it is equal to the heat of solution plus the heat of dilution, but the latter is small and can be ignored. For most food materials, the heat of crystallization is positive, i.e. heat is given out during crystallization. Note that heat of crystallization is the opposite of heat of solution. If a material takes in heat, i.e. has a negative heat of solution, then the heat of crystallization is positive. Heat balances can be calculated for crystallization.

EXAMPLE 9.9. Heat removal in crystallization cooling of lactose

Lactose syrup is concentrated to 8g lactose per l0g of water and then run into a crystallizing vat which contains 2500kg of the syrup. In this vat, containing 2500kg of syrup, it is cooled from 57°C to 10°C. Lactose crystallizes with one molecule of water of crystallization. The specific heat of the lactose solution is $3470 J kg^{-1o}C^{-1}$. The heat of solution for lactose monohydrate is $-15,500\ kJ mol^{-1}$. The molecular weight of lactose monohydrate is 360 and the solubility of lactose at 10°C is 1.5g/l0g water. Assume that 1% of the water evaporates and that the heat loss through the vat walls is $4 x\ 10^4$kJ. Calculate the heat to be removed in the cooling process.

Heat Balance

Heat lost from solution = Heat removed

Sensible heat lost from solution when cooled from 57°C to 10°C + Heat of crystallization

= Heat lost through walls + Latent heat of evaporation + Heat removed by cooling

Heat lost from solution

Sensible heat in solution when cooled from 57°C to l0°C = w x c_s x ΔT

= 2500 x 3.470 x 47

= 40.8 x 10^4kJ

Heat of crystallization

Heat of solution = $15,500 kJmole^{-1}$

= 15,500/360

= $43.1 kJkg^{-1}$

Solubility of lactose at 10°C, 1.5g/l0g water,

Anhydrous lactose crystallized out = (8 - 1.5)

= 6.5 g/ l0gwater

Hydrated lactose crystallized = 6.5 x (342 + 18)/(342)

= 6.8g/l0gwater
Total water = (10/18) x 2500kg
= 1390kg
Total hydrated lactose crystallized out = (6.8 x 1390)/l0
= 945 kg
Total heat of crystallization = 945 x 43.1 kJ
= 4.07 x 10^4 kJ

Heat removed from solution
Heat removed by vat walls = 4.0 x $l0^4$kJ.

Water evaporated = 1% = 13.9kg
The latent heat of evaporation is, from Steam Tables, 2258 kJkg $^{-1}$
Heat removed by evaporation = 13.9x 2258kJ
= 3.14 x $l0^4$kJ.

Heat balance

$$40.8 \times 10^4 + 4.07 \times 10^4 = 4 \times 10^4 + 3.14 \times 10^4 + \text{heat removed by cooling.}$$

Heat removed in cooling = 37.7 x 10^4kJ

Rate of Crystal Growth

Once nucleii are formed, either spontaneously or by seeding, the crystals will continue to grow so long as supersaturation persists. The three main factors controlling the rates of both nucleation and of crystal growth are the temperature, the degree of supersaturation and the interfacial tension between the solute and the solvent. If supersaturation is maintained at a low level, nucleus formation is not encouraged but the available nucleii will continue to grow and large crystals will result. If supersaturation is high, there may be further nucleation and so the growth of existing crystals will not be so great. In practice, slow cooling maintaining a low level of supersaturation produces large crystals and fast cooling produces small crystals.

Nucleation rate is also increased by agitation. For example, in the preparation of fondant for cake decoration, the solution is cooled and stirred energetically. This causes fast formation of nucleii and a large crop of small crystals, which give the smooth texture and the opaque appearance desired by the cake decorator.

Once nucleii have been formed, the important fact in crystallization is the rate at which the crystals will grow. This rate is controlled by the diffusion of the solute through the solvent to the surface of the crystal and by the rate of the reaction at the crystal face when the solute molecules rearrange themselves into the crystal lattice.

These rates of crystal growth can be represented by the equations

$$\mathrm{d}w/\mathrm{d}t = K_d A(c - c_i) \tag{9.13}$$
$$\mathrm{d}w/\mathrm{d}t = K_s A(c_i - c_s) \tag{9.14}$$

where dw is the increase in weight of crystals in time dt, A is the surface area of the crystals, c is the solute concentration of the bulk solution, c_i is the solute concentration at the crystal solution interface, c_s is the concentration of the saturated solution, K_d is the mass transfer coefficient to the interface and K_s is the rate constant for the surface reaction.

These equations are not easy to apply in practice because the parameters in the equations cannot be determined and so the equations are usually combined to give:

$$dw/dt = KA(c - c_s) \qquad (9.15)$$

where

$$1/K = 1/K_d + 1/K_s$$

or

$$dL/dt = K(c - c_s)/\rho_s \qquad (9.16)$$

since

$$dw = A\rho_s dL$$

and dL/dt is the rate of growth of the side of the crystal and ρ_s is the density of the crystal.

It has been shown that at low temperatures, diffusion through the solution to the crystal surface requires only a small part of the total energy needed for crystal growth and, therefore, that diffusion at these temperatures has relatively little effect on the growth rate. At higher temperatures, diffusion energies are of the same order as growth energies, so that diffusion becomes much more important. Experimental results have shown that for sucrose the limiting temperature is about 45°C, above which diffusion becomes the controlling factor.

Impurities in the solution retard crystal growth; if the concentration of impurities is high enough, crystals will not grow.

Stage Equilibrium Crystallization

When the first crystals have been separated, the mother liquor can have its temperature and concentration changed to establish a new equilibrium and so a new harvest of crystals. The limit to successive crystallizations is the build up of impurities in the mother liquor which makes both crystallization and crystal separation slow and difficult. This is also the reason why multiple crystallizations are used, with the purest and best crystals coming from the early stages.

For example, in the manufacture of sugar, the concentration of the solution is increased and then seed crystals are added. The temperature is controlled until the crystal nucleii added have grown to the desired size, then the crystals are separated from the residual liquor by centrifuging. The liquor is next returned to a crystallizing evaporator, concentrated again to produce further supersaturation, seeded and a further crop of crystals of the desired size grown. By this method the crystal size of the sugar can be controlled. The final mother liquor, called molasses, can be held indefinitely without producing any crystallization of sugar.

EXAMPLE 9.10. Multiple stage sugar crystallisation by evaporation
The conditions in a series of sugar evaporators are:

- Entering liquor: concentration 65%, weight 5000kgh^{-1}
- Liquor at seeding: concentration 82%
- First evaporator: temperature of liquor 85°C, concentration of liquor at seeding 82%.
- Second evaporator: temperature of liquor 73°C, concentration of liquor at seeding 84%.
- Third evaporator: temperature of liquor 60°C, concentration of liquor at seeding 86%.
- Fourth evaporator: temperature of liquor 51°C, concentration of liquor at seeding 89%.

Calculate the yield of sugar in each evaporator and the concentration of sucrose in the mother liquor leaving the final evaporator.

SUGAR CONCENTRATIONS (g/100g water)

	On seeding	Solubility	Weight crystallized
First effect	456	385	71
Second effect	525	330	195
Third effect	614	287	327
Fourth effect	809	265	544

The sugar solubility figures are taken from the solubility curve, Fig. 9.8.

MASS BALANCE (weights in kg)
Basis 5000kg sugar solution h^{-1}

	Into effect	At seeding	Sugar crystallized	Liquor from effect
First effect				
Water	1750	713	-	713
Sugar	3250	3250	506	2744
Second effect				
Water	713	522	-	522
Sugar	2744	2744	1018	1726
Third effect				
Water	522	279	-	279
Sugar	1726	1726	912	814
Fourth effect				
Water	279	99	-	99
Sugar	814	814	539	275
Total Sugar			2975	275

Yield in first effect
506kgh^{-1} 506/3250 = 15.6%
Yield in second effect
1018kgh^{-1} 1018/3250 = 31.3%
Yield in third effect
912kgh^{-1} 912/3250 = 28.1%
Yield in fourth effect
539kgh^{-1} 539/3250 = 16.6%
Lost in liquor
275kgh^{-1} 275/3250 = 8.4%
Total yield 91.6%
Quantity of sucrose in final syrup 275 kg/h^{-1}
Concentration of final syrup 73.5% sucrose

Crystallization Equipment

Crystallizers can be divided into two types: crystallizers and evaporators. A crystallizer may be a simple open tank or vat in which the solution loses heat to its surroundings. The solution cools slowly so that large crystals are generally produced. To increase the rate of cooling, agitation and cooling coils or jackets are introduced and these crystallizers can be made continuous. The simplest is an open horizontal trough with a spiral scraper. The trough is water jacketed so that its temperature can be controlled.

An important crystallizer in the food industry is the cylindrical, scraped surface, heat exchanger, which is used for plasticizing margarine and cooking fat, and for crystallizing ice cream. It is essentially a double-pipe heat exchanger fitted with an internal scraper, see Fig. 6.3(c). The material is pumped through the central pipe and agitated by the scraper, with the cooling medium flowing through the annulus between the outer pipes.

A crystallizer in which considerable control can be exercised is the Krystal or Oslo crystallizer. In this, a saturated solution is passed in a continuous cycle through a bed of crystals. Close control of crystal size can be obtained.

Evaporative crystallizers are common in the sugar and salt industries. They are generally of the calandria type. Vacuum evaporators are often used for crystallization as well, though provision needs to be made for handling the crystals. Control of crystal size can be obtained by careful manipulation of the vacuum and feed. The evaporator first concentrates the sugar solution, and when seeding commences the vacuum is increased. This increase causes further evaporation of water which cools the solution and the crystals grow. Fresh saturated solution is added to the evaporator and evaporation continued until the crystals are of the correct size. In some cases, open pan, steam heated, evaporators are still used, for example in making coarse salt for the fish industry. In some countries, crystallization of salt from sea water is effected by solar energy which concentrates the water slowly and this generally gives large crystals.

Crystals are regular in shape: cubic, rhombic, tetragonal and so on. The shape of the crystals forming may be influenced by the presence of other compounds in the solution, even in traces. The shape of the crystal is technologically important because such properties as the angle of repose of stacked crystals and rate of dissolving are related to the crystal shape. Another important property is the uniformity of size of the crystals in a product. In a product such as sucrose, a non-uniform crystalline mixture is unattractive in appearance, and difficult to handle in packing and storing as the different sizes tend to separate out. Also the important step of separating mother liquor from the crystals is more difficult.

MEMBRANE SEPARATIONS

Membranes can be used for separating constituents of foods on a molecular basis, where the foods are in solution and where a solution is separated from one less concentrated by a semi-permeable membrane. These membranes act somewhat as membranes do in natural biological systems.

Water flows through the membrane from the dilute solution to the more concentrated one. The force producing this flow is called the osmotic pressure and to stop the flow a pressure, equal to the osmotic pressure, has to be exerted externally on the more concentrated solution. Osmotic pressures in liquids arise in the same way as partial pressures in gases: using the number of moles of the solute present and the volume of the whole solution, the osmotic pressure can be estimated using the gas laws. If pressures greater than the osmotic pressure are applied to the more concentrated solution, the flow will not only stop but will reverse so that water passes out through the membrane making the concentrated solution more concentrated. The flow will continue until the concentration rises to the point where its osmotic pressure equals the applied pressure. Such a process is called *reverse osmosis* and special artificial membranes have been made with the required "tight" structure to retain all but the smallest molecules such as those of water.

Also, "looser" membranes have been developed through which not only water, but also larger solute molecules can selectively pass if driven by imposed pressure. Membranes are available which can retain large molecules, such as proteins, while allowing through smaller molecules. Because the larger molecules are normally at low molar concentrations, they exert very small osmotic pressures, which therefore enter hardly at all into the situation. Following the resemblance to conventional filtration, this process is called *ultrafiltration*. In general, ultrafiltration needs relatively low differential pressures, up to a few atmospheres. If higher pressures are used, a protein or solute gel appears to form on the membrane, which resists flow, and so the increased pressure may not increase the transfer rate.

Important applications for ultrafiltration are for concentrating solutions of large polymeric molecules, such as milk and blood proteins. Another significant application is to the concentration of whey proteins. Reverse osmosis, on the other hand, is concerned mainly with solutions containing smaller molecules such as simple sugars and salts at higher molar concentrations, which exert higher osmotic pressures. To overcome these osmotic pressures, high external pressures have to be exerted, up to the order of 100 atmospheres. Limitations to increased flow rates arise in this case from the mechanical weaknesses of the membrane and from concentration of solutes which causes substantial osmotic "back" pressure. Applications in the food industry are in separating water from, and thus concentrating, solutions such as fruit juices.

Rate of Flow Through Membranes

There are various equations to predict the osmotic pressures of solutions, perhaps the best known being the van't Hoff equation:

$$\Pi = M\mathrm{R}T \qquad (9.17)$$

in which Π (pi) is the osmotic pressure (kPa), M the molar concentration (moles m^{-3}), T the absolute temperature (^{o}K), and R the universal gas constant. This equation is only strictly accurate when the dilution is infinitely great, but it can still be used as an approximation at higher concentrations.

The net driving force for reverse osmosis is then the difference between the applied differential pressure ΔP, and the differential osmotic pressure, $\Delta\Pi$, which resists the flow in the desired "reverse" direction. Therefore it can be described by the standard rate equation, with the rate of mass transfer being equal to the driving force multiplied by the appropriate mass transfer coefficient:

$$\mathrm{d}w/\mathrm{d}t = KA[\Delta P - \Delta\Pi] \tag{9.18}$$

where $\mathrm{d}w/\mathrm{d}t$ is the rate of mass transfer, K is the mass transfer coefficient, A the area through which the transfer is taking place, ΔP is the net applied pressure developed across the membrane and $\Delta\Pi$ is the net osmotic pressure across the membrane and resisting the flow. ΔP is therefore the difference in the applied pressure on the solutions at each side of the membrane and $\Delta\Pi$ is the difference in the osmotic pressures of the two solutions, as in Fig. 9.9. The gas constant R is 8.314m^{3}kPa mol^{-1} K^{-1}.

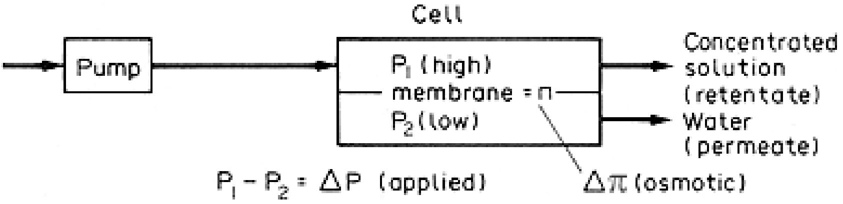


Figure 9.9 Reverse Osmosis System

EXAMPLE 9.11. Concentration of sucrose solution by reverse osmosis

A solution of sucrose in water at 25°C is to be concentrated by reverse osmosis. It is found that, with a differential applied pressure of 5000kPa, the rate of movement of the water molecules through the membrane is 25 kgm^{-2}h^{-1} for a 10% solution of sucrose. Estimate the flow rate through the membrane for a differential pressure of 10,000kPa with the 10% sucrose solution, and also estimate the flow rate for a differential pressure of 10,000 kPa but with a sucrose concentration of 20%. Density of 20% sucrose is 1081kgm^{-3} and for 10% is 1038kgm^{-3}.

For sucrose, the molecular weight is 342 so for a 10% solution, molar concentration is 0.30moles m^{-3} and for 20%, 0.62 moles m^{-3}.

Applying eqn. (9.17):

For 10% solution $\Pi = 0.30 \times 8.314 \times 298$
$= 730\text{kPa}$
For 20% solution $\Pi = 0.62 \times 8.314 \times 298$
$= 1510\text{kPa}$.

So we have for the first case, for 1 m^2 of membrane:

$\mathrm{d}w/\mathrm{d}t = 25 = K[5000 - 753]$
$K = 5.9 \times 10^{-3}\text{kgm}^{-2}\text{ h}^{-1}\text{kPa}^{-1}$
So for $\Delta P = 10{,}000\text{kPa}$,
$\mathrm{d}w/\mathrm{d}t = 5.9 \times 10^{-3}[10{,}000 - 730]$
$= \underline{55\text{kgm}^{-2}\text{h}^{-1}}$

And for $\Delta P = 10{,}000$ and 20% soln.
$\mathrm{d}w/\mathrm{d}t = 5.9 \times 10^{-3}[10{,}000 - 1510]$
$= \underline{50\text{kgm}^{-2}\text{h}^{-1}}$

Experimental values of the osmotic pressure, Π, of the sucrose solutions at 10% and 20% were measured to be 820 and 1900kPa respectively, demonstrating the relatively small error arising from applying the van't Hoff equation to these quite highly concentrated solutions. Using these experimental values slightly reduces the predicted flow as can be seen by substituting in the equations.

In ultrafiltration practice, it is found that eqn. (9.18) applies only for a limited time and over a limited range of pressures. As pressure increases further, the flow ceases to rise, or even falls. This appears to be caused, in the case of ultrafiltration, by increased mechanical resistance at the surface of the membrane due to the build-up of molecules forming a layer which is like a gel and which resists flow through it. Under these circumstances, flow is better described by *diffusion equations* through this resistant layer leading to equation:

$$\mathrm{d}w/\mathrm{d}t \;=\; K'\,A\,\log_e(c_i/c_b) \qquad (9.19)$$

where c_i and c_b are the solute concentrations at the interface and in the bulk solution respectively. The effect of the physical properties of the material can be predicted from known relationships for the transfer coefficient K' (m s^{-1}), which can be set equal to D/δ where D is the diffusivity of the solute ($m^2\ s^{-1}$), divided by δ, the thickness of the gel layer (m). This equation has been found to predict, with reasonable accuracy, the effect on the mass transfer of changes in the physicochemical properties of the solution. This is done through well established relationships between the diffusivity D, the transfer coefficient K', and other properties such as density (ρ), viscosity (μ) and temperature (T) giving:

$$(K'd/D) = a[(\mathrm{d}v\rho/\mu)^m] \times (\mu/\rho D)^n$$

or

$$(\mathrm{Sh}) = (K'd/D) = a\,(\mathrm{Re})^m(\mathrm{Sc})^n \qquad (9.20)$$

where d is the hydraulic diameter, (Sh) the Sherwood number ($K'd/D$); (Sc) the Schmidt number ($\mu/\rho D$); and a, m, n are constants.

Notice the similar form of eqn. (9.20) and the equation for heat transfer in forced convection, $(\mathrm{Nu}) = a\,(\mathrm{Re})^m\,(\mathrm{Pr})^n$, with (Sh) replacing (Nu) and (Sc) replacing (Pr). This is another aspect of the similarity between the various transport phenomena. These ideas, and the uses that can be made of them, are discussed in various books, such as Coulson and Richardson (1977) and McCabe and Smith (1975), and more comprehensively in Bird, Stewart and Lightfoot (1960).

In the case of reverse osmosis, the main resistance arises from increased concentrations and therefore increased back pressure from the osmotic forces. The flow rate cannot be increased by increasing the pressure because of the limited strength of membranes and their supports, and the difficulties of designing and operating pumps for very high pressures.

Membrane Equipment

The equipment for these membrane separation processes consists of the necessary pumps, flow systems and membranes. In the case of ultrafiltration, the membranes are set up in a wide variety of geometrical arrangements, mostly tubular but sometimes in plates, which can be mounted similarly to a filter press or plate heat exchanger. Flow rates are kept high over the surfaces and recirculation of the fluid on the high pressure, or retentate, side is often used; the fluid passing through, called the permeate, is usually collected in suitable troughs or tanks at atmospheric pressure.

In the case of reverse osmosis, the high pressures dictate mechanical strength, and stacks of flat disc membranes can be used one above the other. Another system uses very small diameter (around 0.04mm) hollow filaments on plastic supports; the diameters are small to provide strength but preclude many food solutions because of this very small size. The main flow in reverse osmosis is the permeate.

The systems can be designed either as continuous or as batch operations. One limitation to extended operation arises from the need to control growth of bacteria. After a time bacterial concentrations in the system, for example in the gel at the surface of the ultrafiltration membranes, can grow so high that cleaning must be provided. This can be difficult as many of the membranes are not very robust either to mechanical disturbance or to the extremes of pH which could give quicker and better cleaning.

EXAMPLE 9.12. Ultrafiltration of whey

It is desired to increase the protein concentration in whey, from cheese manufacture, by a factor of 12 by the use of ultrafiltration to give an enriched fraction which can subsequently be dried and used to produce a 50% protein whey powder. The whey initially contains 6% of total solids, 12% of these being protein. Pilot scale measurements on this whey show that a permeate flow of 30kgm^{-2}h^{-1} can be expected. If the plant requirement is to handle 30,000kg in 6 hours, estimate the area of membrane needed. Assume that the membrane rejection of the protein is over 99%, and calculate the membrane rejection of the non-protein constituents.

Protein in initial whey = 6 x 0.12 = 0.72% ≈ 0.7%

Protein in retentate = 12 x concentration in whey
= 12 x 6 x 0.12
= 8.6%.

Setting out a mass balance, basis 100 kg whey:

	Water (kg)	Protein (kg)	Non-protein (kg)	Total (kg)
Initial whey	94.0	0.7	5.3	100.0
Retentate	6.7	0.7	0.7	8.1
Permeate	87.3	0.0	4.6	91.9

Water removed per 100 kg whey = 87.3 kg

The equipment has to process 30,000 kg in 6 h so the membrane has to pass the permeate at:

(30,000 x 91.9)/(100 x 6) = 4595kgh^{-1}

and permeate filtration rate is 30kgm^{-2} h $^{-1}$

Therefore required area of membrane = 4595/30
= $\underline{153\text{m}^2}$

Non-protein rejection = 0.7/5.3
= $\underline{13\%}$

Membrane processes generally use only one apparent contact stage, but product accumulation with time, or with progression through a flow unit, gives situations which are equivalent to multistage units. Dialysis, which is a widely used laboratory membrane processing technique, with applications in industry, sometimes is operated with multiple stages.

These membrane concentration and separation processes have great potential advantages in the simplicity of their operation and because drastic conditions, in particular the use of heat leading to thermal degradation, are not involved. Therefore more extensive application was achieved as membranes, flow systems and pumps were improved. Discussion of these processes can be found in papers by Thijssen (1974) and in Sourirajan (1977).

DISTILLATION

Distillation is a separation process, separating components in a mixture by making use of the fact that some components vaporize more readily than others. When vapours are produced from a mixture, they contain the components of the original mixture, but in proportions which are determined by the relative volatilities of these components. The vapour is richer in some components, those that are more volatile, and so a separation occurs.

In fractional distillation, the vapour is condensed and then re-evaporated when a further separation occurs. It is difficult and sometimes impossible to prepare pure components in this way, but a degree of separation can easily be attained if the volatilities are reasonably different. Where great purity is required, successive distillations may be used.

Major uses of distillation in the food industry are for concentrating essential oils, flavours and alcoholic beverages, and in the deodorization of fats and oils.

The equilibrium relationships in distillation are governed by the relative vapour pressures of the mixture components, that is by their volatility relative to one another. The equilibrium curves for two component vapour/liquid mixtures can conveniently be presented in two forms, as boiling temperature/concentration curves, or as vapour/liquid concentration distribution curves. Both forms are related as they contain the same data and the concentration distribution curves, which are much the same as the equilibrium curves used in extraction, can readily be obtained from the boiling temperature/concentration curves.

A boiling temperature/concentration diagram is shown in Fig. 9.10. Notice that there are two curves on the diagram, one giving the liquid concentrations and the other the vapour concentrations.

If a horizontal (constant temperature) line is drawn across the diagram within the limit temperatures of the two curves, it will cut both curves. This horizontal line corresponds to a particular boiling temperature, the point at which it cuts the lower line gives the concentration of the liquid boiling at this temperature, the point at which it cuts the upper line gives the concentration of the vapour condensing at this same temperature. Thus the two points give the two concentrations which are in equilibrium. They give in fact two corresponding values on the concentration distribution curves, the point on the liquid line corresponding to an x point (that is to the concentration in the heavier phase) and the point on the vapour line to a y point (concentration in the lighter phase). The diagram shows that the y value is richer in the more volatile component of the mixture than *x*, and this is the basis for separation by distillation.

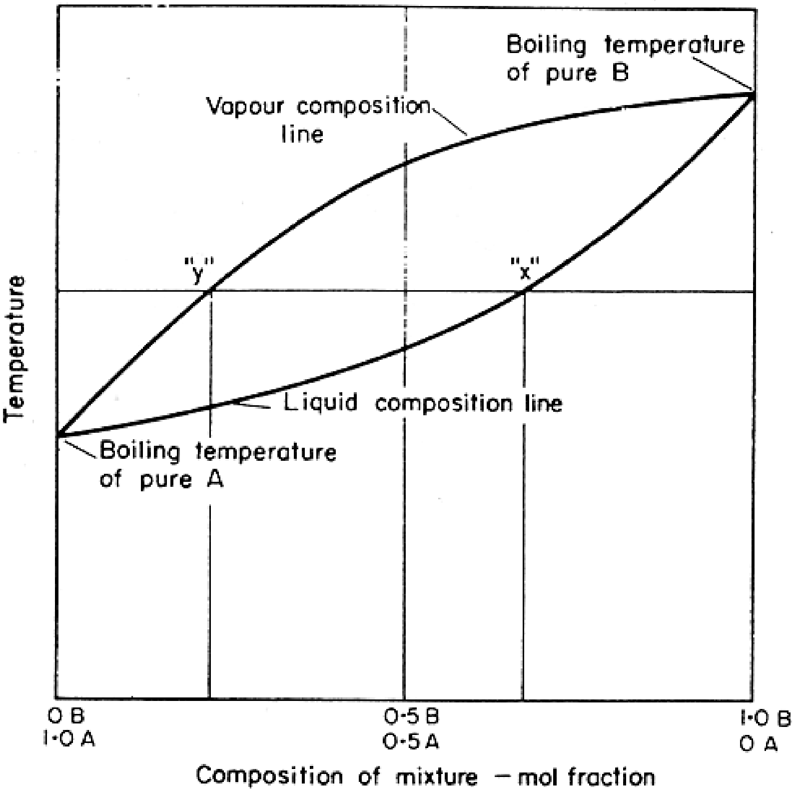


Figure 9.10 Boiling temperature/concentration diagram

It is found that some mixtures have boiling temperature diagrams that are a different shape from that shown in Fig. 9.10. For these mixtures, at another particular temperature and away from the pure components at the extremes of composition, the vapour and liquid composition lines come together. This means that, at this temperature, the liquid boils to give a vapour of the same composition as itself. Such mixtures constitute azeotropes and their formation limits the concentration attainable in a distillation column.

The ethanol/water mixture, which is of great importance in the alcoholic beverage industry, has an azeotrope of composition 89.5mole% (95.6%w/w) ethanol and 10.5 mole% (4.4% w/w) water, at a minimum boiling temperature of 78.15°C. In a distillation column, separating dilute ethyl alcohol and water, the limit concentrations of the streams are 100% water on the one hand in the "liquid" stream, and 95.6% ethyl alcohol, 4.4% water by weight in the "vapour" stream, however many distillation stages are used.

A multi-stage distillation column works by providing successive stages in which liquids boil and the vapours from the stage above condense and in which equilibrium between the two streams, liquid and vapour, is attained. Mass balances can be written for the whole column, and for parts of it, in the same way as with other contact equilibrium processes.

EXAMPLE 9.13. Distillation of alcohol/water mixture

In a single-stage, continuous distillation column used for enriching alcohol/water mixtures, the feed contains 12% of alcohol, and 25% of the feed passes out with the top product (the "vapour" stream) from the still. Given that, at a boiling temperature of 95.5°C, 1.9 mole% of alcohol in the liquid is in equilibrium with 17 mole% of alcohol in the vapour, estimate the concentration of alcohol in the product from the still.

From the equilibrium data given and since the mole fraction of alcohol is small, we may assume a linear equilibrium relationship. The equilibrium curve passes through (0,0) and (1.9, 17) so that over this range we can say $y = x\ (17/1.9)$ or $x = y\ (1.9/17)$ where x is the concentration of alcohol in the liquid and y in the vapour phase.

From the operating conditions given, as the feed is equal to liquid plus vapour phases ($L + V$) we can write:

$$F = L + V$$

and also

$$V = F/4$$

and so

$$F = 4V \text{ and } L = 3V$$

Therefore, for the alcohol, if x_f is the concentration of alcohol in the feed, we can write a mass balance across the distillation column:

$$4Vx_f = 3Vx + Vy$$

The concentration of alcohol in the feed is 12%, which has to be expressed as a mole fraction to be in the same units as the equilibrium data. The molecular weight of alcohol (C_2H_5OH) is 46, and of water 18.

$$x_f = (12/46)/(88/18 + 12/46)$$
$$= 0.05$$

Operating equation:

$$4 \text{ x } 0.05 = 3x + y$$
$$0.2 = 3x + y$$

Equilibrium condition

$$x = (1.9/17)y,$$
$$3(1.9/17)\,y + y = 0.2$$

And so $y = 0.15$mole%

Letting the weight fraction of alcohol in the vapour stream be w we have:

$$0.15 = (w/46)/(w/46 + (1 - w)/18)$$

so $w = 0.31$

$= 31\%$

<u>The concentration of alcohol in product from still = 31%</u>

Continuous fractional distillation columns can be analysed in rather similar ways to continuous extraction systems, They generally have a reboiler at one end of a column and a condenser at the other (head). A feed stream normally enters somewhere away from the end points of the column and there is often provision of reflux, which is a distillate return flow from the condenser section at the head of the column. Full analysis of such columns can be found in standard chemical engineering texts.

Steam Distillation

In some circumstances in the food industry, distillation would appear to be a good separation method, but it cannot be employed directly as the distilling temperatures would lead to breakdown of the materials. In cases in which volatile materials have to be removed from relatively non-volatile materials, steam distillation may sometimes be used to effect the separation at safe temperatures.

A liquid boils when the total vapour pressure of the liquid is equal to the external pressure on the system. Therefore, boiling temperatures can be reduced by reducing the pressure on the system; for example by boiling under a vacuum, or by adding an inert vapour which by contributing to the vapour pressure, allows the liquid to boil at a lower temperature. Such an addition must be easily removed from the distillate, if it is unwanted in the product, and it must not react with any of the components that are required as products. The vapour that is added is generally steam and the distillation is then spoken of as steam distillation.

If the vapour pressure of the introduced steam is p_s and the total pressure is P, then the mixture will boil when the vapour pressure of the volatile component reaches a pressure of $(P - p_s)$, compared with the necessary pressure of P if there were no steam present. The distribution of steam and the volatile component being distilled, in the vapour, can be calculated. The ratio of the number of molecules of the steam to those of the volatile component, will be equal to the ratio of their partial pressures

$$p_A/p_s = (P - p_s)/p_s = (w_A/M_A)/(w_s/M_s) \tag{9.21}$$

and so the weight ratios can be written:

$$w_A/w_S = (P - p_s)/p_s \times (M_A/M_s) \tag{9.22}$$

where p_A *is* the partial pressure of the volatile component, p_s is the partial pressure of the steam, P is the total pressure on the system, w_A is the weight of component A in the vapour, w_s is the weight of steam in the vapour, M_A is the molecular weight of the volatile component and M_s is the molecular weight of steam.

Very often the molecular weight of the volatile component that is being distilled is much greater than that of the steam, so that the vapour may contain quite large proportions of the volatile component.

Steam distillation is used in the food industry in the preparation of some volatile oils and in the removal of some taints and flavours, for example from edible fats and oils.

Vacuum Distillation

Reduction of the total pressure in the distillation column provides another means of distilling at lower temperatures. When the vapour pressure of the volatile substance reaches the system pressure, distillation occurs. With modern efficient vacuum producing equipment, vacuum distillation is tending to supplant steam distillation. In some instances, the two methods are combined in vacuum steam distillation.

Batch Distillation

Batch distillation is the term applied to equipment into which the raw liquid mixture is admitted and then boiled for a time. The vapours are condensed. At the end of the distillation time, the liquid remaining in the still is withdrawn as the residue. In some cases the distillation is continued until the boiling point reaches some predetermined level, thus separating a volatile component from a less volatile residue. In other cases, two or more fractions can be withdrawn at different times and these will be of decreasing volatility. During batch distillation, the concentrations change both in the liquid and in the vapour.

Let L be the mols of material in the still and x be the concentration of the volatile component. Suppose an amount dL is vaporized, containing a fraction y of the volatile component.

Then writing a material balance on component A, the volatile component:

$$y\,dL = d(Lx) = L\,dx + x\,dL$$

$$dL/L = dx/(y - x)$$

and this is to be integrated from L_o moles of material of concentration x_o up to L moles at concentration x.

To evaluate this integral, the relationship between x and y, that is the equilibrium conditions, must be known.

If the equilibrium relationship is a straight line, $y = mx + c$,

$$dL/L = dx/(mx + c - x) = dx/[(m-1)x + c)]$$

then the integral can be evaluated from L_0 to L

$$\text{Ln}\, L/L_0 = \frac{1}{(m-1)}\,\text{Ln}\,[(m-1)x + c] / [(m-1)x_o + c] \qquad (9.23)$$

or

$$L/L_0 = [(y - x)/(y_o - x_o)]^{1/(m-1)}$$

In general, the equilibrium relationship is not a straight line, and the integration has to be carried out graphically. A graph is plotted of x against $1/(y - x)$, and the area under the curve between values of x_0 and x is measured.

Distillation Equipment

The conventional distillation equipment for the continuous fractionation of liquids consists of three main items:

- a boiler in which the necessary heat to vaporize the liquid is supplied,
- a column in which the actual contact stages for the distillation separation are provided,
- a condenser for condensation of the final top product.

A typical column is illustrated in Fig. 9.11.

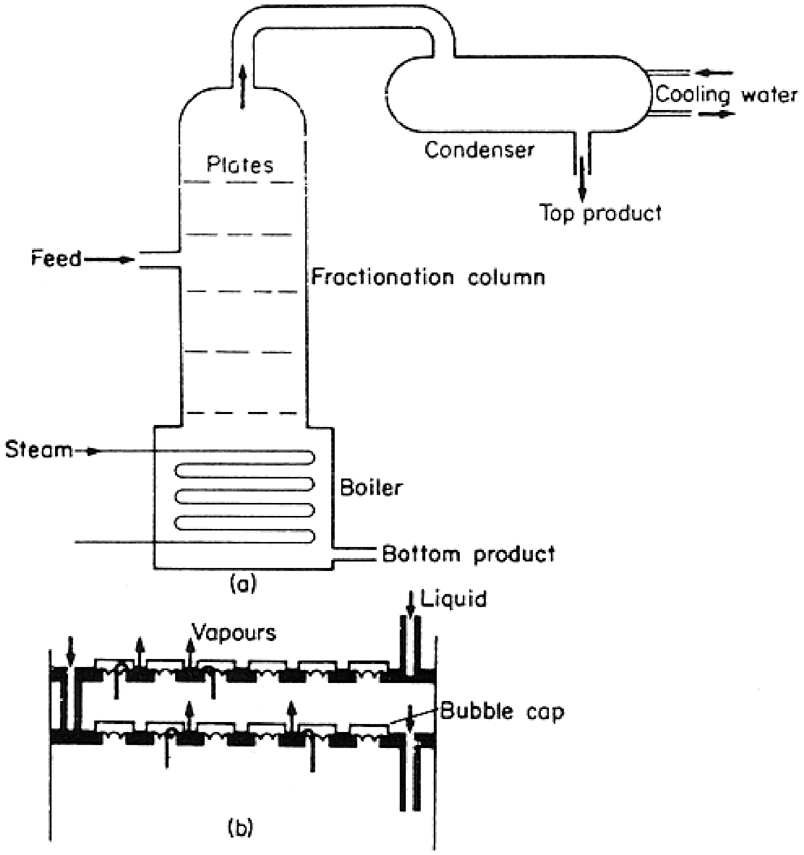


Figure 9.11 Distillation column (a) assembly, (b) bubble-cap trays

The condenser and the boiler are straightforward. The fractionation column is more complicated as it has to provide a series of contact stages for contacting the liquid and the vapour. The conventional arrangement is in the form of "bubble-cap" trays, which are shown in Fig. 9.11(b). The vapours rise through the bubble caps. The liquid flows across the trays past the bubble caps where it contacts the vapour and then over a weir and down to the next tray. Each tray represents a contact stage, or approximates to one as full equilibrium is not necessarily attained, and a sufficient number of stages must be provided to reach the desired separation of the components.

In steam distillation, the steam is bubbled through the liquid and the vapours containing the volatile component and the steam are passed to the condenser. Heat may be provided by the condensation of the steam, or independently. In some cases the steam and the condensed volatile component are immiscible, so that separation in the condenser is simple.

SUMMARY

1. The equilibrium concentrations of components of mixtures often differ across the boundary between one phase and another. Such boundaries occur between liquid and solid, liquid and vapour, between immiscible liquids, and between liquids or gases separated by membranes.

2. These differences can be used to effect separations by the enrichment of one phase relative to the other, by differential transfer of mass of particular components across the phase boundary.

3. Rates of mass transfer across the phase boundaries are controlled by the differences between actual concentrations and equilibrium concentrations, which constitute the mass transfer driving force, and by resistances which impede transfer. Therefore the rate of mass transfer is very generally determined by a driving force and by a mass-transfer coefficient.

$$\mathrm{d}w/\mathrm{d}t = kA(c - c_{equilibrium})$$

4. Analysis of mass-transfer-contact-equilibrium systems is carried out by comparing the equilibrium conditions to the actual conditions in the system; and using the difference, together with material conservation relationships that describe the movements within and between the phases, to follow the transfer of mass.

5. The analysis can be carried out systematically, relating equilibrium conditions and material balance (or operating) conditions, and energy balances, over single and multistage systems.

PROBLEMS

1. The composition of air is 23 % oxygen, 77% nitrogen by weight, and the Henry's Law constant for oxygen in water is 3.64×10^4 atm mole fraction^{-1} at 20°C. Calculate the solubility of oxygen in water (a) as the mole fraction and (b) as a percentage by weight.
   ((a) 0.056×10^{-4} mole fraction (b) 0.00103%)

2. If in the deodorizer of worked Example 9.5, relative flow rates of cream and steam are altered to 1:1, what will be the final concentration of the taint in the cream coming from a plant with three contact stages?
   (0.05ppm)

3. Casein is to be washed, in a multistage system, by water. The casein curd has initially a water content of 60% and between stages it is drained on an inclined screen to 80% water (both on a wet basis). The initial lactose content of the casein is 4.5 % on a wet basis, and it is necessary to produce casein with a lactose content of less than 1 % on a dry basis. How many washing steps would be needed if the wet casein is washed with twice its own weight of fresh water in each step?

(3washing steps reduce to 0.56% on a dry basis)

4. Estimate the osmotic pressure of a solution of sucrose in water containing 20% by weight of sucrose. The density of this solution is 1081 kgm^{-3} and the temperature 20^oC.
   (1540kPa)

5. In a six-step sugar-boiling crystallization process, the proportions of the sucrose present removed in the successive crystallizations are 66.7%, 60%, 60%, 50%, 50% and 33%. If the original sugar was associated with 0.3% of its weight of non-sucrose solids, calculate (a) the percentage of non-sucrose material in the dry solids of the final molasses and (b)the proportion of the original sugar that remains in the molasses. Assume that after each crystallization, all of the impurities remain with the mother liquor.
   ((a) 25% (b) 0.89%)

6. For a particular ultrafiltration plant concentrating skim milk, for a concentration ratio of 7:1 of protein relative to lactose, the plant capacity is $570kgm^{-2}\ h^{1}$ of skim milk. Assume that this is the flow rate through the membrane. Estimate (a)the plant capacity at a concentration ratio of 2:1 and the percentage of the water in the skim milk removed by the ultrafiltration.
   ((a) $1600kgm^{2}h^{-1}$ (b) 50%)