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### **MIXTURES**

A mixture is a system that is analysed in terms of two or more different entities; e.g. air can be taken as a mixture of nitrogen and oxygen (but can be taken as a pure substance if composition does not change in the problem at hand); oxygen itself can be taken as a natural mixture of 99.8 % atoms of isotope  $^{16}\text{O}$  and 0.2 % of isotope  $^{18}\text{O}$ ; a fully-ionised plasma can be taken as a mixture of ions and electrons; the contents of a commercial butane bottle can be taken as a mixture of liquid and vapour, each one being a mixture of butane and propane; etc. We analyse here mixtures of simple non-reacting chemical substances that form a single phase or a multiphase system, but that they exchange species between phases or with the environment. [Chemically reacting mixtures](#) are covered separately.

Most substances found in nature are mixtures of pure chemical elements or compounds: air, natural gas, seawater (but also tap water), coffee, wine, gasoline, antifreeze, body fluids, etc. The reason for this widespread occurrence is that there is a natural tendency for entropy to increase in the mixing (although energy minimisation might work against, as in liquid vapour equilibrium under gravity). Thus, some exergy has to be applied to a mixture to separate its components. Furthermore, some exergy is also applied in many practical cases to accelerate the natural mixing process, notably by mechanical stirrers, vibrations and ultrasounds, or electromagnetic forcing; in flow systems, nozzles, swirls, colliding jets, or pulsating injectors are commonly used for the same purpose. The mixing time may be short in gases (we soon detect the smell of an open perfume flask), long in liquids (who waits for sugar to dissolve in a coffee cup), or extremely long in solids (stained glass holds its metal-oxide nano-particles, which give their vivid colours, dispersed in the glass matrix for centuries).

Mixtures usually form multiphasic systems except when the components are perfectly miscible (notably gas/gas mixtures, and some liquid/liquid mixtures like ethanol/water), or when, having some miscibility gap, the mixture is unsaturated.

### Saturated states

In thermodynamics, a saturated state is a multiphasic equilibrium state. When phase changes in pure substances were studied, saturated vapour, saturated liquid and saturated solid, were considered. For mixtures, saturation (with respect to one of its components) is the point at which the mixture can dissolve no more of that substance (e.g. water saturated with sugar is the sugar/water solution in equilibrium with sugar, air saturated with water vapour is the water/air mixture in equilibrium with liquid water, and so on).

Unsaturated mixtures can become saturated by addition of more substance, or by just changing temperature or pressure at constant composition. Notice that there are some mixtures that cannot get saturated, as mentioned above.

### Standard thermodynamic states

Thermodynamic properties of a mixture depend on temperature, pressure, and composition. When analysing mixture behaviour, and when property data are tabulated, some standard thermodynamic state is chosen as reference ('standard' just means established by authority or custom).

- Temperature standard: the mean sea level air temperature,  $T_0=288.15$  K (15 °C), should be the preferred standard, but  $T^\ominus=298.15$  K (25 °C) is the most used temperature reference in thermochemistry, and so we adopt it when studying [Chemically reacting mixtures](#), and other standard values are also used in some other context: e.g. 0 K (a limit used in ideal gas models), 273.15 K (0 °C; a most simple reproducible state), and 293.15 K (20 °C, a comfort working environment). The effect of temperature in a mixture is difficult to model except for the perfect substance model (i.e. ideal gases or ideal liquids, with constant thermal capacity,  $c_p$ ).
- Pressure standard: the mean sea level pressure  $p_0=10^5$  Pa (1 bar), is the preferred standard, but  $p_0=1.01325$  bar (1 atm, 101.325 Pa) was the traditional standard before 1982, and is still used (the difference is often negligible). When real gas behaviour is to be analysed in terms of the ideal gas model, the standard thermodynamic state at  $p_0=10^5$  Pa is not the real value at  $p_0=10^5$  Pa but the extrapolation of the ideal model ( $p \rightarrow 0$ ) up to  $p_0=10^5$  Pa. The effect of pressure in a mixture is simple to model except for very large pressures: gas-mixtures behaviour is proportional to pressure, and liquid-mixture behaviour is nearly independent of pressure.
- Composition standard: the usual reference state for any chemical species in a mixture is its pure chemical substance, but when solids or gases are dissolved in liquid solvents, the reference state for these solutes is the infinite dilution property (i.e. when its molar fraction is very small,  $x_s \rightarrow 0$ ) extrapolated to unitary molar concentration, although 1 mol/L is most often used instead of the strict SI unit 1 mol/m<sup>3</sup>, infinite dilution (often extrapolated to 1 mol/L). The effect of composition in a mixture is difficult to model except for the ideal mixture model presented below.

We only consider ideal mixtures below; real mixtures are based on ideal mixture models and '[excess functions](#)'; ideal [solutions](#) (a kind of real mixture amenable to simple modelling), and some important real [solution properties](#), can be found aside.

## HOMOGENEOUS-MIXTURES

We start by considering homogeneous mixtures, i.e. we consider a homogeneous system formed by coming into intimate contact two or more different homogeneous systems; i.e. a heterogeneous system that becomes a homogeneous system when mixed. So we say that water and air do not mix, water and oil neither, but water and alcohol certainly do. However, it is difficult to distinguish a mixture from a fine [dispersion](#) (e.g. oil and water shaken, milk, water and air in a cloud). Homogeneous systems have particle size below  $d=10^{-9}$  m, and their properties are independent of size for systems of size above  $L=10^{-7}$  m, although in the nano-range, ( $10^{-9}..10^{-7}$ ) m, their behaviour is size-dependent.

The easiest mixtures to deal with are gaseous mixtures: gases readily mix (as noticed when distant odours enter our nostrils). The most important gaseous mixtures are humid air (dry air plus water vapour), fuel gases (natural gas, town gas, liquefied petroleum gases), and combustion gases (fuel/air and exhaust mixtures). The thermodynamics of gaseous mixtures is rather simple: an ideal mixture has a weighted average of their perfect-gas component properties (some corresponding state models may be used to account for non-ideal behaviour). An additional feature is the limit of solubility of vapours in a gaseous mixture (e.g. how much water vapour may mix with a certain amount of nitrogen).

Liquid mixtures may be formed from two liquids (e.g. water and ethanol), from a liquid and a gas that dissolves in the liquid, or from a liquid and solid that dissolves in the liquid. In most cases one liquid is preponderant and is called the solvent, and the rest of substances (gases, liquids and solids) are called solutes, the mixture being named [solution](#). The thermodynamics of liquid mixtures is usually rather complex, except for mixtures of similar-molecule liquids (e.g. hydrocarbons), where an ideal model similar to a gas mixture can be applied. In most cases, however, there are energetic and volumetric effects and some '[excess functions](#)' must be added to the thermodynamic formulation (these non-ideal behaviour may be used to produce [hot pads and cold pads](#)). Detailed analysis of [solutions](#) can be found aside. The limits of solubilities are very difficult to predict; for instance, at 15 °C, sugar can only dissolve in water up to 65 % by weight in the syrup, salt can only dissolve in water up to 35 % by weight in the brine, air can only dissolve in water up to 10 ppm massive in nitrogen and 10 ppm in oxygen (note that oxygen dissolves better). Moreover, contrary to a gas mixture, a liquid mixture may appear in more than one liquid phase, given rise to a fluid interface (e.g. oil and water mixtures) as in liquid/gas two-phase systems. On top of that, some solutes (solid, liquid or gas) dissociate more or less into ions (electrolytes) when mixed with some liquids, notably water, giving rise to complex electrochemical effects (see [Solutions](#)).

Solid mixtures (e.g. metal/metal, wax/wax) have so little mobility (except at very high temperatures) that they are usually processed in the molten state (i.e. as liquid mixtures).

Under the influence of external force fields like gravity, centrifugation or electromagnetic fields, all mixtures settle (see [Mixture settling](#)), but we here assume, as implicitly done in two-phase mixtures of pure substances, that they are either unsettled or perfectly settled (e.g. gas phase over liquid phase).

### Mixture specification

The state of a pure substance is fixed by temperature and pressure. The state of a multi-component system requires additional variables to specify the composition. The variance of a system, or Gibbs phase rule,  $V=2+C-P$ , was analysed in detail in [Chapter 2: Entropy](#). For single phase mixtures ( $P=1$ ),  $V=2+C-1$ , i.e., besides temperature and pressure, as many intensive composition-parameters as the number of components minus one (e.g. just one factor for a binary mixture).

The basic property of a single-phase mixture is its composition, which may be specified by different parameters, the most usual being:

$$\text{molar fractions: } x_i \equiv \frac{n_i}{\sum n_i} = \frac{y_i / M_i}{\sum y_i / M_i} \quad (7.1)$$

$$\text{mass fractions: } y_i \equiv \frac{m_i}{\sum m_i} = \frac{x_i M_i}{\sum x_i M_i} \quad (\text{Note: present SI symbol is } w_i) \quad (7.2)$$

$$\text{mass densities: } \rho_i \equiv \frac{m_i}{V} = y_i \rho \quad (7.3)$$

$$\text{molar densities or concentrations: } c_i \equiv \frac{n_i}{V} = \frac{\rho_i}{M_i} = \frac{x_i}{\sum x_i M_i} \rho \quad (7.4)$$

The molar mass of the mixture is:

$$M \equiv \frac{m}{n} = \sum x_i M_i = \frac{1}{\sum \frac{y_i}{M_i}} \quad (7.5)$$

Molar variables are favoured in the analysis of mixtures, because experience shows that mixture behaviour is in many cases proportional to the number of particles (proportional to the amount of substance), and not to other physical characteristic or attributes as their mass. Properties that really behave in that way are called colligative properties, several of them being covered at the end of this chapter.

It is here assumed that mixture composition is prescribed. The problem of finding the qualitative or quantitative composition in a mixture is known as chemical analysis, or just analysis, using techniques that may be grouped as:

- Chemical methods of analysis, mainly referring to the old “wet techniques” and other classical methods: characteristic reactions, titration, selective absorption, liquid or gas chromatography (the most widespread analytical technique), etc.

- Physical methods of chemical analysis, ranging from the omnipresent balance, to the most sophisticated radiometric and spectroscopic techniques, and including the thermal methods of chemical analysis (e.g. scanning calorimetry and fractional distillation).

Many times, a sample of the mixture is analysed off-line and discarded, often through a separation process of chromatography, but most advanced analytical techniques are non-intrusive and on-line.

### Ideal mixture model

The aim of mixture modelling is to provide a mixture-property model in terms of some pure-substance-property model and some generic mixing model, to avoid the need for experimental data for all the variety of compositions.

The most restrictive thermodynamic model of a mixture is called the ideal mixture model, IMM, which assumes that volumetric and energetic properties of a mixture are just the linear combination of those of their pure constituents (weighted with their relative proportions), and that mixing entropy only depends on proportions (and not on material properties). All the components of an ideal mixture at a given  $T$  and  $p$  must be in the same phase when pure: e.g. at 15 °C and 100 kPa, nitrogen and oxygen in air, water and methanol in liquid phase, but not nitrogen and water or water and salt.

For a pure substance we learn that a full set of data for the equilibrium states was (Chapter 4):  $v=v(T,p)$  and  $c_p=c_p(T,p_0)$ . The ideal mixture model assumes:

$$v(T, p, x_i) = \sum x_i v_i^*(T, p) \quad (7.6)$$

$$c_p(T, p_0, x_i) = \sum x_i c_{p_i}^*(T, p_0) \quad (7.7)$$

i.e. the molar volume of the mixture is the averaged molar volume of the pure components (the \* is meant to recall 'pure substance'), and similarly for any other additive conservative property (e.g.  $h(T,p,x_i)=\sum x_i h_i^*(T,p)$ ). To check the validity of the IMM model one can measure all the terms in (7.6) and compute the excess molar volume (and similarly for the energies). Notice that (7.6-7) could also be stated as  $v(T,p,y_i)=\sum y_i v_i^*(T,p)$  and  $c_p(T,p,y_i)=\sum y_i c_{p_i}^*(T,p)$  if now all the  $v$ 's and  $c_p$ 's are specific volume and specific thermal capacities, instead of molar volumes and molar thermal capacities, but this cannot be extrapolated (e.g.  $M=\sum x_i M_i \neq \sum y_i M_i$ , mixing entropies depend directly on  $x_i$  but not on  $y_i$ , and so on).

Entropy however, although it is additive and thence  $s(T,p,x_i)=\sum x_i s_i(T,p,x_i)$  ( $s_i$  being the partial molar entropy  $s_i \equiv \partial S / \partial n_i$ ), it is not conservative, it increases on mixing, and thus we have:

$$v(T, p, x_i) = \sum x_i v_i^*(T, p) \quad (7.6)$$

$s(T,p,x_i)=\sum x_i s_i^*(T,p)+\Delta s_{\text{mixing}}$ . Within the ideal mixture model, this entropy increase is directly obtained from (2.1) with probabilities to find a molecule of species  $i$  being proportional to its molar fraction (and changing the constant  $k$ , per molecule, to the constant  $R$ , per mol); i.e.:

$$\Delta s_{\text{mixing}} = -R \sum x_i \ln x_i \quad (7.8)$$

Thus, the molar entropy of mixing in an ideal mixture, is just a geometric factor of species distribution, and do not depends on the nature of the substances. Real entropies of mixing are computed from the absolute entropies of the components and the actual mixture ([Chapter 9: Thermodynamics of chemical reactions](#)).

The Gibbs function is not conservative either, and for an ideal mixture one gets:

$$\begin{aligned} g(T, p, x_i) &= h - Ts = \\ &= \sum x_i h_i^*(T, p) - T(\sum x_i s_i^*(T, p) - R \sum x_i \ln x_i) = \sum x_i g_i^*(T, p) + RT \sum x_i \ln x_i \end{aligned} \quad (7.9)$$

what serves to get the explicit dependence of chemical potentials on composition for an ideal mixture, since, from (4.4):

$$g(T, p, x_i) = \sum \mu_i n_i / n = \sum x_i \mu_i \rightarrow \mu_i(T, p, x_i) = \mu_i^*(T, p) + RT \ln x_i \quad (7.10)$$

where  $\mu_i^* = h_i^* - Ts_i^*$ . Recall that, in general,  $\mu_i$  not only depends on  $x_i$  but on the other molar fractions  $x_j$  in the mixture, and that the algebraic value of  $\mu_i$  (sign and absolute value) is of little interest because it depends on these other mixture parameters, but, in a natural (spontaneous) process,  $\mu_i$  decreases.

To get the explicit dependence of chemical potential on temperature and pressure we use Maxwell relations (equality of second crossed derivatives) from  $dG = -SdT + Vdp + \sum \mu_i dn_i$  to get:

$$\left. \frac{\partial \mu_i}{\partial p} \right|_{T, n_i} = \left. \frac{\partial V}{\partial n_i} \right|_{T, p} = v_i \begin{cases} \stackrel{\text{PLM}}{=} \frac{M_i}{\rho_{Li}} \Rightarrow \mu_i(T, p, x_i) = \mu_i^\oplus(T, p^\oplus) + \frac{p - p^\oplus}{\rho_{Li} / M_i} + RT \ln x_i \\ \stackrel{\text{PGM}}{=} \frac{RT}{p} \Rightarrow \mu_i(T, p, x_i) = \mu_i^\oplus(T, p^\oplus) + RT \ln \frac{p}{p^\oplus} + RT \ln x_i \end{cases} \quad (7.11)$$

$$\left. \frac{\partial \mu_i}{\partial T} \right|_{T, n_i} = \left. \frac{-\partial S}{\partial n_i} \right|_{T, p} = -s_i \Rightarrow g_i = \mu_i = h_i - Ts_i = h_i + T \left. \frac{\partial \mu_i}{\partial T} \right|_{T, n_i} \Rightarrow \left. \frac{\partial \mu_i}{\partial T} \right|_{T, n_i} = h_i \quad (7.12)$$

where  $\oplus$  refers to an arbitrary reference state that for ideal mixtures coincides with the state of the pure substance at conditions  $T$  and  $p^\oplus$  (see [Excess functions](#) for the more general case).

The ideal mixture model can be widened if, instead of the values of pure substances at the same  $T$  and  $p$  conditions, one considers in (7.6-7) the values for pure substances at some ideal states as  $T$  and  $p \rightarrow 0$  (see Liquid-vapour mixtures).

It is good time now to recall that for a system to be in equilibrium, its temperature must be uniform, its velocity field must correspond to a solid-body motion, and its chemical potential has to verify

$\mu_i + M_i g z - \frac{1}{2} M_i (\vec{\Omega} \times \vec{r})^2 = \text{constant}$ . In the study of mixtures one usually assumes the absence of external force fields, and thence the chemical potential is also uniform at equilibrium, but an example follows of how to deal with external force fields.

### [Exercise 1. Change in composition of dry air with height](#)

#### **Real mixtures**

Real mixtures deviate more or less from this simple ideal-mixture model. For gaseous mixtures, the approximation may be good enough for not-too-high pressures, but for liquid and solid mixtures it may deviate so much that this ideal model must be corrected with so called [excess functions](#)).

For gaseous mixtures, perhaps the simplest non-ideal mixture model is using a non-ideal equation of state with its parameters average-weighted with those of the pure components; e.g. using van der Waals equation of state,  $(p+a/v^2)(v-b)=RT$ , with constants  $a=\sum x_i a_i$  and  $b=\sum x_i b_i$ , or the corresponding state model with  $T_{cr}=\sum x_i T_{cr,i}$  and  $p_{cr}=\sum x_i p_{cr,i}$ ; the latter is known as Kay's rule, and the former is usually enhanced by the virial mixing rule for the energy term,  $a=\sum \sum x_i x_j a_{ij}$ , with  $a_{ii}=a_i$  and  $a_{ij}$  for  $i \neq j$  being additional cross-correlations parameters (the linear rule for the volume term,  $b=\sum x_i b_i$ , is good enough in most circumstances, so there is no need for a quadratic mixing rule as for the energy term).

#### **Exergy of demixing**

One of the basic goals of Chemical Engineering is to produce valuable substances by separation from their mixtures, reaction with their ores, or synthesis from other substances. Furthermore, most chemical-analysis methods rely on a first stage of mixture separation (notably gas or liquid chromatography), followed by detection and quantification of the isolated species, although modern spectrometric methods may perform a direct non-intrusive analysis.

Mixture separation (demixing) may be performed by different processes: by gravity or centrifugal sedimentation, by flowing through porous-plugs (chromatography) or selective membranes (see at the end), by phase change (distillation, precipitation, diffusion to an immiscible liquid), by ionisation and application of electric or magnetic fields (mass spectrography), by absorption with selective synthetic zeolites, by absorption in a supercritical fluid (high solubility) that desorbs at low pressure, by electrochemical purification (concentration fuel cells), etc. Already in the 4th century b.C. Aristotle wrote: "Salty water, when it turns into vapour, becomes sweet, and the vapour does not form salt water when it condenses again. This is known by experiment".

We do not intend to go on with any particular method, but to consider just the thermodynamic limit of minimum energy required to accomplish a demixing (all practical processes will need more energy, which would be computed with the appropriate energy balance once the details are given). A common demixing process is dehumidification (removing water vapour from air; see [Humid air](#)).

Exergy was introduced in Chapter 3, and the general expression for the exergy of a system at equilibrium in the presence of an infinite atmosphere, deduced to be (3.9). The exergy balance for a control volume was presented in (5.5), and, once chemical composition is accounted for, yield:

$$\Delta\Phi = \Delta(E + p_0V - T_0S)_{n_i} + \sum n_i(\mu_i - \mu_{i0})_{T_0, p_0} = W_u + \int \left(1 - \frac{T_0}{T}\right) dQ - T_0S_{gen} + \sum^{\text{openings}} \int \psi_e \dot{n}_e dt \quad (7.13)$$

with the molar exergy of flow:

$$\psi \equiv (h - T_0s)_{n_i} + \sum x_i(\mu_i - \mu_{i0})_{T_0, p_0} \quad (7.14)$$

Equations 7.13-14 are the general expressions for the exergy of a mixture, but we want to solve first the most basic problem of how much work is required to separate a gaseous component of the ambient gaseous atmosphere. The answer follows from (7.14): the first parenthesis is nil because no temperature or pressure variation would take place for minimum work, and for the difference in chemical potential (7.10) is used, resulting in that the exergy of a pure gaseous component is:

$$\psi_{i0} = -RT_0 \ln x_{i0} \quad (7.15)$$

e.g. getting pure oxygen from air costs a minimum of  $-8.3 \cdot 288 \cdot \ln 0.21 = 3.7$  kJ/mol. Notice that this energy cost is not associated to working against any attractive force to extract the oxygen molecules (particles are non-interacting in the ideal gas model); it is a genuine entropy contribution without global energy change (21 mol of O<sub>2</sub> plus 79 mol N<sub>2</sub>, at  $T_0$  and  $p_0$ , have the same energy either mixed or unmixed; the mixing process is with  $\Delta E = W + Q = 0$ ,  $W = 0$ ,  $Q = 0$ ,  $\Delta S > 0$ ,  $\Delta G < 0$ , i.e. a natural process, whereas the ideal demixing process would be with  $\Delta E = W + Q = 0$ ,  $W > 0$ ,  $Q < 0$ ,  $\Delta S < 0$ ,  $\Delta G > 0$ , i.e. an artificial process).

For (7.15) to be valid, the species must remain in the same phase after separation at  $T_0$  and  $p_0$ , what is not the case for water vapour since at 15 °C and 100 kPa it is liquid, if pure. But the computation may be done in two parts: first a separation to pure gas at  $T_0$  and  $p^*(T_0)$ , and afterwards a pressure variation (with phase change) from  $p^*(T_0)$  to  $p_0$ , with the result:

$$\psi_{i0} = -RT_0 \ln x_{i0} + RT_0 \ln \frac{p^*(T_0)}{p_0} + \frac{p_0 - p^*(T_0)}{\rho_L / M} \approx -RT_0 \ln \frac{x_{i0} p_0}{p^*(T_0)} \quad (7.16)$$

In the next chapter we will see that the argument of the last logarithm is precisely the relative humidity.

### [Exercise 2. Air fractionation](#)

Exergy being a state function, it means that the maximum obtainable work from a given pure component and the atmospheric mixture is precisely the same; e.g. if one had a flow of pure oxygen at thermal and mechanical equilibrium with the atmosphere, one might get 3.7 kJ per mol of oxygen, by returning it to atmospheric mixture through an appropriate non-consuming device. However unreal this problem may



sound for the oxygen/air universe, consider that the same applies to the problem of pure water / salt water universe that is readily available at any river mouth, and projects have already been thought to profit from it.

## LIQUID-VAPOUR MIXTURES

It is clear that the first stage in the study of mixtures is to restrict ourselves to binary mixtures. Sometimes this two-component model is even applicable to mixtures of many more chemical species, as when humid air is treated as a binary mixture of dry air (a multicomponent mixture itself) and water vapour. Some other times, however, even starting with only two species, as  $\text{H}_2\text{O}$  and  $\text{NaCl}$ , the system gets ternary by the formation of new chemical compounds (hydrates or anhydrous) in the mixture.

When a gaseous binary mixture is cooled (temperature decreases at constant pressure and composition), point P in Fig. 7.1, liquid drops eventually appear of a liquid mixture of different composition, P', than the rest of the gas, P'. That difference in composition is the basics of distillation, the process of separating components in a mixture by natural phase-change segregation.

In binary mixtures it is usual to name only one molar fraction,  $x$ , the other being  $1-x$ . In fact, the molar fraction  $x$  in the abscissa may refer to the total molar fraction of the selected species  $i$ ,  $x_i$ , to the molar fraction in the liquid phase,  $x_{L,i}$ , or to the molar fraction in the vapour phase,  $x_{V,i}$ . Contrary to pure substances, mixtures do not show a single condensation temperature (for a given pressure), but a range of temperatures from the first drop appearing (condensation curve) to the last bubble remaining (boiling curve), except when an azeotrope is formed (Fig. 7.1).

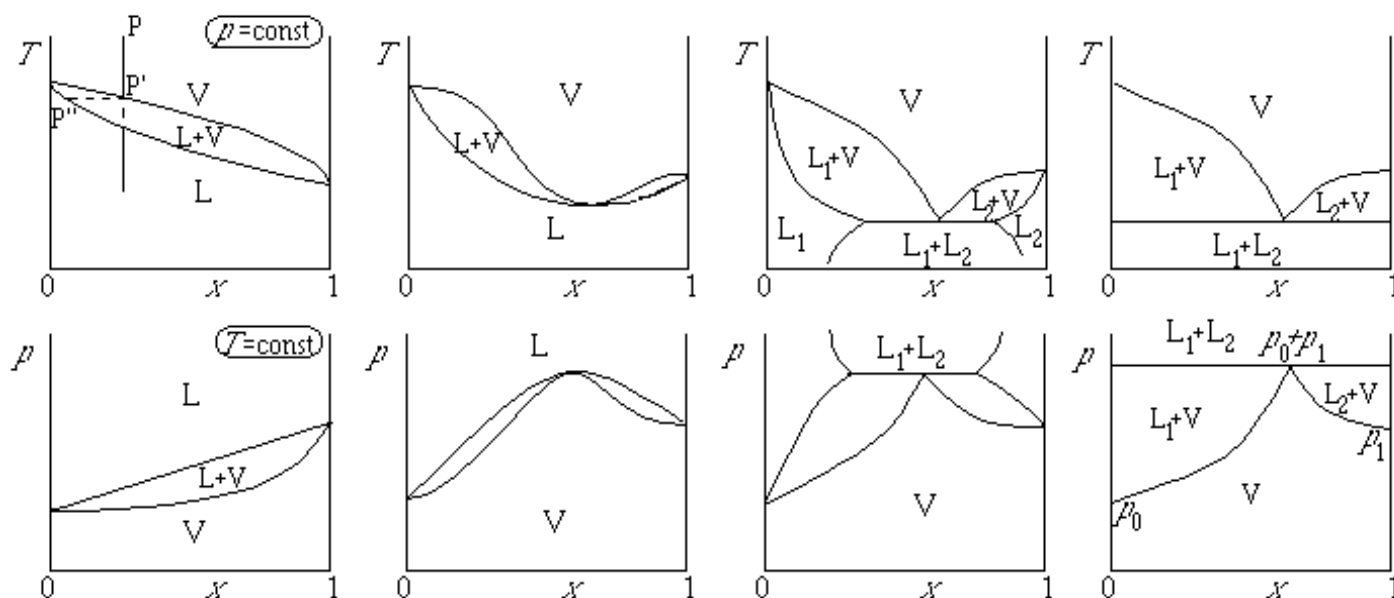


Fig. 7.1. Temperature vs. molar fraction at constant pressure (upper row), and pressure vs. molar fraction at constant temperature (lower row), for binary mixtures of different substances with different types of solubility, from ideal mixtures that perfectly mix (left) to insoluble liquids (right). A liquid mixture that boils at constant temperature (as a pure substance, retaining also the composition) is called an azeotrope (e.g. water and ethanol have an azeotrope for 95.6% by mass ethanol).

Plotting condensation and boiling curves for different real substances yields the different diagrams depicted in Fig. 7.1, ranging from a perfect mixture (the ideal mixture model above defined), to a mixture of insoluble liquids, through partial solubility mixtures with azeotrope. If the molecular attraction of components A and B in the mixture is much larger than both A-A and B-B, the boiling-point curve shows a maximum (azeotrope), and have negative enthalpy of mixing and negative excess volume (e.g. water/nitric-acid mixtures have  $T_{az}=120$  °C while  $T_{b,water}=100$  °C and  $T_{b,nitric}=87$  °C), whereas if the molecular attraction of components A and B in the mixture is much smaller than both A-A and B-B, the boiling-point curve shows a minimum (azeotrope), and have positive enthalpy of mixing and positive excess volume (e.g. water/ethanol mixtures have  $T_{az}=78.2$  °C while  $T_{b,water}=100$  °C and  $T_{b,ethanol}=78.4$  °C).

Similar behaviour occurs when pressure is increased in a gaseous binary mixture at constant temperature and composition (Fig. 7.1 lower row). However, only  $T$ - $x$  diagrams are used in liquid-solid phase diagrams because pressure has little influence on condensed phases.

Although liquid-solid phase diagrams may be similar to Fig 7.1, for dissimilar substances (e.g. iron and carbon, as for steels), much more involved phase diagrams appear, with several allotropic phases and formation of compounds. A relevant feature in such diagrams is the eutectic point, corresponding to the minimum melting point of an alloy. Liquid-vapour phase diagrams are much used in chemical engineering, and solid-liquid diagrams in metallurgy and geology. Some [solid-liquid phase diagrams can be found aside](#).

### Ideal liquid-vapour mixtures. Raoult's law

For the study of binary liquid-vapour mixtures we extend the ideal mixture model defined by equations 7.6-7 in the following way. For the temperature of the mixture, the pressure in the mixture may be above the two vapour pressures of the pure components (both would be liquid if pure), below both (both would be gas if pure), or in between. Computation of energy and entropy changes for mixing or demixing in the two former cases is trivial (Eq. 7.8), and for temperature and pressure changes without phase change also (e.g. ideal gas model or ideal liquid model); the only difficulty is when a phase change would occur if the mixture were separated at constant temperature and pressure. But we could circumvent this problem by first changing the pressure in the mixture to go outside the two-phase region and then separate, what teaches that the same ideal mixture model may be applied but assuming that the pure components remain in the phase they have in the mixture. If we consider an ideal gas reference state ( $p \rightarrow 0$ ) for each component, Equations 7.6-7 are substituted for a two-phase mixture by:

$$\text{gas phase: } v_v(T, p, x_i) = \sum x_i \frac{RT}{p} \quad (7.18)$$

$$\text{liquid phase: } v_L(T, p, x_i) = \sum x_i \frac{M_i}{\rho_{Li}(T)} \quad (7.19)$$

$$\text{gas phase: } h_v(T, p, x_i) = \sum x_i c_{pvi} (T - T^\ominus) \quad (7.20)$$

$$\text{liquid phase: } h_L(T, p, x_i) = \sum x_i \left[ c_{pvi} (T^\ominus - T_{bi}) - h_{LVbi} - c_{Li} (T_{bi} - T) \right] \quad (7.21)$$

where its own normal boiling point ' $b_i$ ' is used for the phase-change of each component  $i$ . It must be mentioned that the ideal mixture model may give a poor approximation to mixture densities in the liquid state (for a binary liquid mixture, Eq. (7.19) becomes  $M_L/\rho_L=x_{L1}M_1/\rho_{L1}+x_{L2}M_2/\rho_{L2}$ , with  $M_L=x_{L1}M_1+x_{L2}M_2$  being the liquid mixture molar mass), and the simpler rough interpolation  $\rho_L=x_{L1}\rho_{L1}+x_{L2}\rho_{L2}$  may yield better results.

Restricting the analysis to ideal binary mixtures, the liquid-vapour equilibrium at given  $T$  and  $p$  requires the equality of the chemical potentials in each phase for each component; for component 1:

$$\begin{aligned}\mu_{L1}(T, p, x_{L1}) &= \mu_{V1}(T, p, x_{V1}) = \\ &= \mu_{L1}^{\oplus}(T, p^{\oplus}) + RT \ln x_{L1} + \frac{p - p^{\oplus}}{\rho_{L1}/M_1} = \mu_{V1}^{\oplus}(T, p^{\oplus}) + RT \ln x_{V1} + RT \ln \frac{p}{p^{\oplus}}\end{aligned}\quad (7.22)$$

where (7.10-11) have been used. Choosing as reference the pressure at which the chemical potential of the pure vapour equals that of the pure liquid (i.e. the vapour pressure of component 1 pure:  $p_1^*$ ), neglecting the pressure term in the liquid phase, and combining the logarithms, one gets what is known as Raoult's law:

$$\frac{x_{V1}}{x_{L1}} = \frac{p_1^*(T)}{p}\quad (7.23)$$

that may be read as follows: a component 1 in a two-phase binary mixture dissolves in the vapour-phase proportional (not linearly) to temperature, and dissolves in the liquid phase proportionally to pressure.

And similarly for the other component:

$$\frac{1 - x_{V1}}{1 - x_{L1}} = \frac{p_2^*(T)}{p}\quad (7.24)$$

To know the state of a two-phase binary system at given  $T$  and  $p$ , the composition of both phases can be found with Eqs. (7.23-24). To know the proportion of each phase we need some global variable, usually the overall composition measured by the global molar fraction of one component,  $x_{01}$ , i.e. the amount of substance 1 in all phases (0 stands for 'all phases') divided by the total amount of all substances, and thence:

$$x_{01} = x_{V1}x_{V0} + x_{L1}(1 - x_{V0}) \quad \text{and} \quad 1 - x_{01} = (1 - x_{V1})x_{V0} + (1 - x_{L1})(1 - x_{V0})\quad (7.25)$$

where  $x_{V0}$  ( $x_{L0}=1-x_{V0}$ ) is the molar fractions in the vapour phase (defined as the total amount of substance in this phase, '0' now stands for 'all components', divided by the total amount of substance in the system).

From the global molar volume of the two-phase binary mixture,  $v=x_{L0}v_L+x_{V0}v_V$ , the global density  $\rho$  can be found,  $M/\rho=x_{L0}M_L/\rho_L+x_{V0}M_V/\rho_V=x_{L0}M_L/\rho_L+x_{V0}RT/p$ , or, assuming the two molar masses of the same order of magnitude, and the same for liquid densities and gas densities, the straightforward relation

$1/\rho = x_{L0}/\rho_L + x_{V0}/\rho_V$ , since, with these assumptions, molar fractions are equal to mass fractions. Notice however that the direct interpolation  $\rho = x_{L0}\rho_L + x_{V0}\rho_V$ , is not applicable to two-phase mixtures (it can only be applied to the liquid state, as said before); however,  $\rho = \phi_L\rho_L + \phi_V\rho_V$  is valid if the  $\phi$ 's are volume fractions instead of mass or molar fractions.

It can be easily shown that, for a given input set  $(T, p, x_{01})$ , the system of 3 equations (7.23-25) with 3 unknowns  $(x_{V1}, x_{L1}, x_{V0})$  reduce to a single equation in  $x_{V0}$ :

$$\frac{(K_1 - 1)x_{01}}{x_{V0}(K_1 - 1) + 1} + \frac{(K_2 - 1)(1 - x_{01})}{x_{V0}(K_2 - 1) + 1} = 0, \quad \text{with } K_i \equiv \frac{x_{Vi}}{x_{Li}} = \frac{p_i^*(T)}{p} \quad i = 1..2 \quad (7.26)$$

i.e., a second order polynomial in  $x_{V0}$  that has a solution only if  $K_1$  and  $K_2$  are at different sides of unity. After solving (7.26) for  $x_{V0}$ , the others,  $x_{V1}$  and  $x_{L1}$ , are obtained from (7.23-24).

It is not difficult to generalise (7.26) to any multi-component non-ideal mixture in vapour-liquid equilibrium:

$$\sum_{i=1}^C \frac{(K_i - 1)x_{0i}}{x_{V0}(K_i - 1) + 1} = 0, \quad \text{with } K_i \equiv \frac{x_{Vi}}{x_{Li}} \quad i = 1..C \quad (7.27)$$

what is known as Rachford-Rice equation, where the  $K$ -values for each component, defined as the ratio of molar fraction in the vapour phase divided by molar fraction in the liquid phase, must be also supplied as input data for non-ideal mixtures, whereas they are given by the pressure quotient in (7.26) for ideal mixtures. Once  $x_{V0}$  is found from (7.27),  $x_{Vi}$  and  $x_{Li}$  are obtained from:

$$x_{Li} = \frac{x_{0i}}{x_{V0}(K_i - 1) + 1}, \quad x_{Vi} = K_i x_{Li}, \quad i = 1..C \quad (7.28)$$

Coming back to ideal binary mixtures, another usual problem is to find the condensation point for a given gaseous mixture when cooled at constant pressure or compressed at constant temperature, or conversely, to find the boiling point for a given liquid mixture when heated at constant pressure or expanded at constant temperature. The equations to solve are:

$$\text{Condensation: } \frac{x_{01}}{x_{L1}} = \frac{p_1^*(T)}{p}, \quad \frac{1 - x_{01}}{1 - x_{L1}} = \frac{p_2^*(T)}{p} \quad (7.29)$$

$$\text{Boiling: } \frac{x_{V1}}{x_{01}} = \frac{p_1^*(T)}{p}, \quad \frac{1 - x_{V1}}{1 - x_{01}} = \frac{p_2^*(T)}{p} \quad (7.30)$$

In the  $T$ - $x$  diagram both curves (condensation and boiling) are exponential because of the  $p^*(T)$ -term, but in the  $p$ - $x$  diagram the boiling curve is a straight line, as can be easily deduced:

$$\text{Boiling at a given } T: \quad px_{V1} + p(1 - x_{V1}) = p = p_1^*(T)x_{01} + p_2^*(T)(1 - x_{01}) \quad (7.31)$$

### [Exercise 3. Liquid air composition](#)

### [Exercise 4. Butane bottle](#)

The study of liquid vapour mixtures is substantial to most chemical applications. As a matter of fact, the traditional chemical icon is the distiller, in spite of being a physical process without chemical change. The still or alembic was first used in Alexandria (Egypt) during the Hellenistic period; the head of the pot was called ambix (Gr. head of the still), and in the 7th c. the Arabs named the distillers Al-Ambiq.

Distillation, evaporation, and drying technologies, are thermally-driven energy-intensive processes, accounting for some 50 %, 20 %, and 10 % of the industrial separations energy consumption. It is important to keep in mind that distillation can not only be forced by heating (as in the traditional alembic) but by flashing into vacuum or at least a pressure below the saturation pressure of the feed liquid. For instance the traditional means of making drinking water in a vessel was to flash seawater through an orifice into a chamber kept under vacuum by a seawater ejector; inside the chamber, a heat exchanger heated with the main-engine cooling water vaporises the brine, and a heat exchanger cooled with seawater condenses the vapours; two pumps extract the distillate and the residual brine. Reverse osmosis desalination systems are, however, replacing nowadays vacuum distillation systems.

#### **Dilute liquid-gas mixtures. Henry's law**

When a liquid and a gas enter into contact, temperature and, in absence of external force-fields, pressure and chemical potential of each species, must equilibrate, what implies that some gas-component must dissolve into the liquid phase, and that some liquid-component must evaporate into the gas phase, attaining a liquid-vapour equilibrium similar to the one just studied, but which does not respond to the ideal mixture model; we distinguish them by calling this one liquid-gas equilibrium (and we change the phase name accordingly, from V to G); besides, we identify the two components separately, the liquid one as 'dis' (or solvent; from dissolve) and the gas one as 's' (for solute).

The liquid-gas equilibrium is formulated in a similar manner as the liquid-vapour equilibrium; Eq. (22) now takes the form, for the originally-liquid species, 'dis':

$$\begin{aligned}\mu_{L,\text{dis}}(T, p, x_{L,\text{dis}}) &= \mu_{G,\text{dis}}(T, p, x_{G,\text{dis}}) = \\ &= \mu_{L,\text{dis}}^{\oplus}(T, p^{\oplus}) + RT \ln x_{L,\text{dis}} + \frac{p - p^{\oplus}}{\rho_{L,\text{dis}} / M_{\text{dis}}} = \mu_{G,\text{dis}}^{\oplus}(T, p^{\oplus}) + RT \ln x_{G,\text{dis}} + RT \ln \frac{p}{p^{\oplus}} \\ \Rightarrow \ln \frac{x_{L,\text{dis}} p^{\oplus}}{x_{G,\text{dis}} p} &= \frac{\mu_{G,\text{dis}}^{\oplus}(T, p^{\oplus}) - \mu_{L,\text{dis}}^{\oplus}(T, p^{\oplus})}{RT} - \frac{p - p^{\oplus}}{\rho_{L,\text{dis}} / M_{\text{dis}}}\end{aligned}\quad (7.32)$$

which, choosing  $p^{\oplus}$  equal to the equilibrium vapour pressure of the solvent,  $p^{\oplus} = p_{\text{dis}}^*(T)$ , cancels the first term in the right-hand-side of (7.32), what leads to Raoult equation if we neglect the pressure-effect on the liquid, as before:

$$\ln \frac{x_{L,\text{dis}} p_{\text{dis}}^*(T)}{x_{G,\text{dis}} p} = 0 \quad (7.33)$$

However, equilibrium for the originally-gas species, 's' leads to:

$$\begin{aligned}
 \mu_{L,s}(T, p, x_{L,s}) &= \mu_{G,s}(T, p, x_{G,s}) = \\
 &= \mu_{Ldis,s}^{\infty}(T, p) + RT \ln x_{L,s} = \mu_{G,s}^{\oplus}(T, p^{\oplus}) + RT \ln x_{G,s} + RT \ln \frac{p}{p^{\oplus}} \\
 \Rightarrow \ln \frac{x_{L,s} p^{\oplus}}{x_{G,s} p} &= \frac{\mu_{Ldis,s}^{\infty}(T, p) - \mu_{G,s}^{\oplus}(T, p^{\oplus})}{RT} \quad (7.34)
 \end{aligned}$$

which cannot be cancelled because  $\mu_{Ldis,s}^{\infty}$  is not the potential of species 's' in its pure liquid state but its potential in an infinitely diluted solution of solvent 'dis' (that is why subindex L was changed to Ldis). Consequently, Raoult's law no longer applies to the gas solute, but, as pressure-effects in condensed phases can be neglected, the right-hand-side of (7.34) is just a function of temperature, and (7.34) can be written as:

$$\ln \frac{x_{L,s} p^{\oplus}}{x_{G,s} p} = \ln K_{s,dis}^{xp}(T), \quad \text{or} \quad \ln \frac{c_{L,s}}{c_{G,s}} = \ln K_{s,dis}^{cc}(T), \quad \text{with} \quad \frac{c_{L,s}}{c_{G,s}} = \frac{x_{L,s}}{x_{G,s}} \frac{\rho_{L,m} RT}{M_{L,m}} \quad (7.35)$$

where  $c$ 's are molar concentrations,  $\rho_{L,m}$  and  $M_{L,m}$  the density and molar mass of the liquid mixture,  $R$  the universal gas constant, and  $K_{s,dis}^{xp}$  and  $K_{s,dis}^{cc}$  (and several others that could be defined in similar ways using different variables and thus having different values and units), are loosely called Henry's constants (they depend on temperature), in honour of W. Henry, who in 1803 was the first to notice that gases dissolve in liquids proportionally to the applied pressure (before Raoult developed in 1883 the theory of ideal solutions). [Values of Henry's law constants and further details of solutions can be found aside.](#)

Raoult's and Henry's laws may be written in terms of the equilibrium partial pressures in the gas phase,  $p_{i,G}$ , corresponding to a molar fraction dissolved,  $x_{i,L}$ , in the short form (good as a mnemonic):

$$p_{i,G} = p_i^*(T) x_{i,L} \quad (\text{Raoult's law}) \quad (7.36)$$

$$p_{i,G} = H_i(T) x_{i,L} \quad (\text{Henry's law}) \quad (7.37)$$

where  $H_i(T)$  is just another instance of 'Henry constant',  $H_i(T) = p_i^{\oplus} / K_{s,dis}^{xp}$ .

### Dilute liquid-solid mixtures

When a liquid and a solid enter into contact, temperature and, in absence of external force-fields, pressure and chemical potential of each species, must equilibrate, what implies that some solid-component must dissolve into the liquid phase, and that some liquid-component must diffuse into the solid phase, attaining a liquid-solid equilibrium similar to the liquid-vapour equilibrium studied above, but which does not respond to the ideal mixture model. If we identify the two components separately as before, the liquid one as 'dis' (or solvent; from dissolve) and the solid one as 's' (for solute), the liquid-solid equilibrium is formulated in a similar manner as the liquid-vapour equilibrium; Eq. (7.22) now takes the form, for the

originally-solid species, 's', that dissolves (the originally-liquid species, 'dis', has so little mobility in the solid phase that in most circumstances it can be assumed non-diffusing or not at equilibrium):

$$\begin{aligned}
 \mu_{L,s}(T, p, x_{L,s}) &= \mu_{S,s}(T, p, x_{S,s}) = \\
 &= \mu_{Ldis,s}^{\infty}(T, p) + RT \ln x_{L,s} = \mu_{S,s}^*(T, p) \\
 \Rightarrow \ln x_{L,s} &= \frac{\mu_{Ldis,s}^{\infty}(T, p) - \mu_{S,s}^*(T, p)}{RT}
 \end{aligned} \tag{7.38}$$

which, as before, cannot be cancelled because  $\mu_{Ldis,s}^{\infty}$  is not the potential of species 's' in its pure liquid state but its potential in an infinitely diluted solution of solvent 'dis' (that is why subindex Ldis was used instead of L). The right-hand-side of (7.38) is just a function of temperature since pressure-effects in condensed phases can be neglected, but it does not receive a special name.

When dissolving ionic solids (and other polar covalent molecules in any phase state) into polar liquids, there is a splitting of part of the solute molecules into its component ions, what gives way to electrolytic solutions.

[Values for the equilibrium functions of solubility, and further details of solutions can be found aside.](#) The main idea to keep in mind is that the thermodynamic model for non-ideal mixtures require additional data on top of the pure-component-data, but there is some underlying structure in the data; e.g. the variation of solute solubility with temperature is directly related to the enthalpy of solution, as the variation of vapour pressure is directly related to the enthalpy of vaporization in pure substances.

## ENERGY AND EXERGY OF IDEAL MIXTURES

We now want to know how much energy is needed to heat a multiphase mixture, and how much work is needed to separate a multiphase mixture or change its composition.

Energy, for an ideal two-phase mixture, is just the simple addition of the energies of every component in every phase; by unit of total amount of substance:

$$h(T, p, x_{ij}) = x_{V0} (x_{V1} h_{V1} + x_{V2} h_{V2}) + x_{L0} (x_{L1} h_{L1} + x_{L2} h_{L2}) \tag{7.39}$$

where the enthalpies are from (7.18-21), whereas the entropy is:

$$s(T, p, x_{ij}) = x_{V0} (x_{V1} s_{V1} + x_{V2} s_{V2} + \Delta s_{\text{mixing}_V}) + x_{L0} (x_{L1} s_{L1} + x_{L2} s_{L2} + \Delta s_{\text{mixing}_L}) \tag{7.40}$$

where the entropies for the pure substances in the appropriate phase are computed in a similar manner as (7.18-21), and the entropies of mixing are always (7.8) since the mixing and demixing may always be done outside of the coexistence two-phase region.

Equation 7.39 teaches that the energy needed to perform a complete phase change at constant pressure, from a saturated liquid mixture at the boiling temperature  $T_b$ , to a saturated vapour mixture at the condensation temperature  $T_c$  (with the same composition) is:

$$\Delta h_{LV} = (x_1 h_{V1} + x_2 h_{V2}) - (x_1 h_{L1} + x_2 h_{L2}) = \sum x_i [c_{Li}(T_{bi} - T_b) + h_{LVbi} + c_{pvi}(T_c - T_{bi})] \quad (7.41)$$

and also teaches that the isobaric thermal capacity during the phase change (that for pure substances was infinite), for a two-phase binary mixture is:

$$c_{p_{mix}}(T, p, x_{ij}) = \frac{dh}{dT} \quad (7.42)$$

where  $h$  is given by (7.39), but taking into account that all the  $x$ 's in (7.39) change with temperature according to (7.23-25). The result is that the isobaric thermal capacity during two-phase boiling is very high (inversely proportional to the temperature span for complete boiling), but finite.

## MEMBRANE SEPARATION

The major industrial separation technologies are: distillation, evaporation, drying, extraction, absorption, adsorption, crystallization, membrane, floatation and sieve screening. All flow restrictions (membranes, porous media, valves, bends) introduce flow disturbances dependent more or less on the molecular structure of the species flowing, what may be used for their separation; i.e. all membranes are selective in some degree. Membrane characteristics and usage are summarised in Table 1.

Table 1. Membrane characteristics and usage according to size of pores.

$10^{-10}..10^{-9}$ m	$10^{-9}..10^{-8}$ m	$10^{-8}..10^{-7}$ m	$10^{-7}..10^{-6}$ m	$10^{-6}..10^{-5}$ m	$10^{-5}..10^{-4}$ m
Reverse osmosis	Nanofiltration	Ultrafiltration	Microfiltration	Microfiltration	Particle filtration
Acetate or polyamide membranes	Acetate, polyamide or polyvinyl alcohol	Polysulfonated, polyacrylic, ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	Polymers or ceramics	Polymers or ceramics	Ceramics
Electron microscope			Optical microscope		
Atoms, ions and molecules <0.2 kg/mol	Large molecules <20 kg/mol	Macro-molecules ~100 kg/mol	Small living-cells	Bacteria	Spores, pollen
Gases, water, mineral ions	Dialysis, sugar, antibiotics	Proteins, viruses, soot	Pigment, smoke	Fog, dust (flour, talc, ash)	Hair, mist, very fine sand
$\Delta p > 10\ 000$ kPa yield $> 10^{-6}$ m/s	$\Delta p > 1000$ kPa $> 10^{-5}$ m/s	$\Delta p > 100$ kPa $> 10^{-6}$ m/s	$\Delta p > 10$ kPa $> 10^{-4}$ m/s	$\Delta p > 1$ kPa $> 10^{-3}$ m/s	$\Delta p < 1$ kPa $> 10^{-2}$ m/s

Basically, microfiltration is centred around the micrometer, and nanofiltration around the nanometer. All practical membranes are 0.15 mm thick or more, although the active layer may be less than 1  $\mu$ m beyond microfiltration, and their pore size distribution must be according to the filtration wanted; beyond ultrafiltration however, the affinity between membrane material and solvent has great influence. Electrodialysis makes use of membranes that are selective to one type of electrical charge (two



membranes of conjugated selectivity are needed to have a neutral separation); it is used to desalinate brackish (low salinity) waters, and to remove urea and uric acid from blood in kidney patients (haemodialysis). Reverse osmosis, introduced in 1920 by Manegold, is at present the preferred method of water desalination (it was multistage flash vaporisation, in the last third of the 20th c.), from the smallest domestic-size to the largest utility-size (e.g. the Carboneras plant at Almería, Spain, where 12 turbopumps 2.5 MW each, deliver 3.1 m<sup>3</sup>/s at 7 MPa through 12 000 spiral-type membranes, yielding 1.4 m<sup>3</sup>/s of pure water, less than 0.4 kg/m<sup>3</sup> of total dissolved solids, at a price of 15 MJ/m<sup>3</sup>).

## COLLIGATIVE PROPERTIES

Amongst the properties of mixtures that only depend on total amount of substance and not of their types, one has (only valid for ideal mixtures):

$$\text{Pressure of a gas mixture: } p = \sum n_i RT / V \quad (7.43)$$

$$\text{Vapour pressure with a solute: } p_v = p_v^*(1 - x_s) \quad (7.44)$$

$$\text{Boiling point with a solute: } T_b = T_b^* + \frac{RT_b^{*2}}{h_{LV}} x_s \quad (7.45)$$

$$\text{Freezing point with a solute: } T_f = T_f^* - \frac{RT_f^{*2}}{h_{SL}} x_s \quad (7.46)$$

$$\text{Osmotic pressure with a solute: } p = p^* + n_s RT / V \quad (7.47)$$

The deduction of these equations, by simply establishing the equality of chemical potentials, is left for the exercises.

Most of these colligative properties can be used to characterise a species in a mixture (e.g. to find the molar mass of a solute from the change in melting or boiling point of the mixture, from the osmotic pressure, etc.). [Further details of solutions can be found aside.](#)

## TYPE OF PROBLEMS

Besides housekeeping problems of how to deduce one particular equation from others, the types of problems in this chapter are:

1. Find the gradient in composition in the equilibrium of a mixture in an external force field.
2. Find the minimum required work to separate a component from a mixture.
3. Find distribution of substance in a two-phase binary mixture.
4. Determine concentrations (or even molar masses if the concentration is known) from colligative properties.

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