THERMODYNAMICS OF SOLUTIONS

Solutions quantification

Mixtures and solutions

A mixture is any multi-component system, i.e. one with several chemical species. The thermodynamics of mixtures in general (gaseous, liquid or solid) has been considered under the heading Mixtures, mainly devoted to ideal mixtures. The term 'solution' is mostly used for the special case of a mixture between very dissimilar components, i.e. when a small amount of substance, called solute (solid, liquid or gas), dissolves to a certain limit in a liquid or solid substance (pure, or a mixture itself) called the solvent. In many solutions of interest, the sum of the mole fractions of the solutes is small compared to unity, and the solution is called a dilute solution. We assume true solutions, i.e. homogeneous solutions, and do not consider colloids and suspensions, treated under the heading Mixture settling. Reacting mixtures are covered in Chemical reactions, aside.

Most solutions depart from the ideal-mixture-model developed in Mixtures, but it is important to recall the basic result from the multiphase equilibrium of ideal mixtures, i.e. Raoult's law for ideal vapour-liquid-equilibrium (VLE):

$$\frac{x_{i,gas}}{x_{i,liq}}=\frac{p_i^*(T)}{p}\quad\text{(for ideal mixtures)}\qquad(1)$$

i.e., for any component *i*, its molar fraction in the vapour phase, $x_{i,gas}$, is to its molar fraction in the liquid phase, $x_{i,liq}$, as its pure-component vapour-pressure at that temperature, $p_i^*(T)$, is to the actual pressure, *p*.

If a solution behaves as an ideal mixture, Raoult's law for each component in a binary mixture of solute 's' in solvent 'dis', in terms of solute mole fractions would read:

$$\frac{x_{s,gas}}{x_{s,liq}}=\frac{p_s^*(T)}{p}\quad\text{and}\quad\frac{1-x_{s,gas}}{1-x_{s,liq}}=\frac{p_{dis}^*(T)}{p}\qquad(2)$$

which can be approximately solved in the following limits like that:

$$\text{for }\ p_{dis}^*>>p_s^*\ \text{(e.g. salts in water)}\quad\frac{x_{s,gas}}{x_{s,liq}}=\frac{p_s^*(T)}{p_{dis}^*(T)}<<1\quad\text{and}\quad p=p_{dis}^*\left(1-x_{s,liq}\right)\quad(3)$$

$$\text{for }\ p_{dis}^*<<p_s^*\ \text{(e.g. gases in water)}\quad\frac{x_{s,liq}}{x_{s,gas}}=\frac{p_{dis}^*(T)}{p_s^*(T)}<<1\quad\text{and}\quad p=p_s^*\left(1-x_{s,liq}\right)\quad(4)$$

with the following interpretation:

- when a non-volatile solute dissolves in a liquid, (3), it lowers the solvent VLE-pressure, and its fraction on the vapour phase is proportional to its vapour pressure when pure (negligible);
- when a very-volatile solute dissolves in a liquid (4), it lowers the solute VLE-pressure, and its fraction on the liquid phase is proportional to the vapour pressure of the pure solvent (small).

Solutions are everywhere: seawater (but also tap water), coffee, soda, wine, vinegar, gasoline, antifreeze, body fluids (e.g. human plasma is roughly an 8%wt proteins plus 1% salts in water, milk serum is roughly a 5%wt lactose plus 3% proteins in water, urine is roughly a 2.5%wt urea plus 2%wt salts in water), etc. Milk may appear to be a homogeneous mixture to the unaided eye, but the tiny oil and protein droplets in the system make milk to appear white (milk is a colloid). Sea water contains many ions in addition to sodium and chloride ions; when gradually evaporated, the first salt to precipitate is $CaCO_3$ (present to the extent of 0.12 g/L), followed by $CaSO_4{\cdot}H_2O$ (1.75 g/L), then NaCl (29.7 g/L), $MgSO_4$ (2.48 g/L), $MgCl_2$ (3.32 g/L), NaBr (0.55 g/L), and KCl (0.53 g/L).

Solvents should be inert (not react with solutes), volatile (low boiling point, to ease distillation), and recyclable. They are usually grouped as:

- Polar solvents (water, methanol, ammonia). Polar solvents are hydrophilic, usually H-bond donors (like water itself, the most important solvent by far), or through hydroxyl groups as in ethanol (CH_3-CH_2OH), or through carboxylic groups like in acetic acid (CH_3-COOH). Polarity is measured by the dielectric constant. Some polar solvents are organic, notably acetone (they are not H-bond donors).
- Non-polar solvents (benzene, toluene, ether, hexane, carbon tetrachloride, trichloromethane (chloroform), methylene chloride, gasoline, mineral oil). Most organic solvents, greatly used in the chemical and biochemical industries (food and pharmacy), are harmful to health and the environment, and are being replaced by supercritical fluids. 'Dry cleaning' is not dry at all; it is said dry because the liquid is not soaking water by a volatile solvent (usually 1,1,2,2-tetrachloroethene). Carbon dioxide is a non-polar fluid, but has poor solvent properties outside supercritical conditions.
- Supercritical fluids (carbon dioxide, ethane, trifluoromethane (fluoroform), sulfur hexafluoride, di-nitrogen oxide (nitrous oxide), carbon disulphide). Supercritical fluids show a dissolving power quickly increasing with pressure (up to a limit). Pure supercritical carbon dioxide is a relatively non-polar solvent, but has some limited affinity with polar molecules due to its large molecular quadri-pole, although modifiers (e.g. methanol, fluorinated hydrocarbons) can be added to improve the solubility of polar molecules. Supercritical water becomes totally miscible with many organic compounds like heptane and benzene. An advantage of supercritical solvents is that they yield the dry solute by simple evaporation of the solvent. The range for supercritical applications is p/p_{CR}=1..2 and T/T_{CR}=1.0..1.1.

The main solvent is water, and thus most solutions are aqueous solutions. Most solutes are solid powders (e.g. salt-water solutions). Water scarcely dissolves gases and organic liquids, and liquid-liquid solutions may be considered plain mixtures; that is why the basic understanding of ‘to dissolve’ is to untie a solid to become part of a liquid. It is the solvent that pulls the solute into solution, and its internal motion (diffusion and convection) what spreads the solute around. Some details on mixing can be found aside in Mass transfer and in Chemical kinetics.

Usually, solutes do not dissolve on the solvent vapour (i.e. they are usually non-volatile), neither on the solvent solid phase (they do not fit into the crystalline lattice). Both mentioned-processes can be used to get rid of solutes (e.g. salt water becomes fresh water when vaporised or solidified), at least when done carefully, but, in practice, solutes can be entrained by solvent-vapours (mainly as an aerosol of particles) and can be trapped within the solid solvent (at the seashore, one may feel salty lips just from the marine breeze, and some ice may taste salty too).

All solutions have some stratification of composition at equilibrium, as studied in Mixture settling. Besides, solution tend to change the composition with time in open systems, i.e. in solutions open to the atmosphere or when the solution is blooded someway, since the escape will not have the same average composition; e.g. the composition inside a liquefied-petroleum-gas bottle changes during use, becoming richer in the heavier components, as well as within a liquefied-natural-gas tanker, due to the boil-off.

The relative amount of solute in a solution (its concentration) may be measured by different concentration variables related amongst them (but not always in a trivial manner); since all solutions depart from ideal (Raoult's law) mixtures, the use of molar quantities for the solvent is rare (molar quantities were an advantage for modelling ideal mixtures because, in that case, the behaviour is just proportional to the molar composition, independently of the actual substances involved).

Concentration specification

One of the main difficulties in the study of solutions is the wide variety of variables and units used to specify concentration (in the case of ideal mixtures, only molar fractions, and sometimes mass fractions, were common). Generically speaking, concentrations in a mixture express the quantitative composition (although, under the SI standard, composition must refer to the unit volume of the system, i.e. mol/m^3, kg/m^3). The subject gets obscure also by the lack of a clear nomenclature, e.g. to distinguish with a letter from 'solution' (we will use subscript *m*, from mixture), 'solute' (we will use subscript *s*, from solute) and 'solvent' (we will use subscript *dis*, from dissolve); the standard labelling of '1' for solute and '2' for solvent, may be unclear when one wants to distinguish between solvent and solution.

To give an idea of the variety of variables used, consider the following values for oxygen-solubility in water (all of them valid under certain circumstances): 39 mg/kg, 0.039 kg/m^3, 1.2 mol/m^3, 22 ppm, 4.6 ppm, 0.26 mol/m^3, 8.2 mg/L, 5.9 mL/L, 55 mL/L, to name a few. And, fortunately, oxygen solubility is so small that the value is the same by amount of solution than by amount of solvent. The explanation of the above figures is that 78 mg/kg is equal to 78 mg/L for aqueous solutions where 1 L has 1 kg; it is also equal to 78/32=2.4 mol/m^3; and it is also equal to 22 parts per million molar, but these values refer to concentration of dissolved oxygen in equilibrium with pure oxygen at 25 ºC and 100 kPa (a common physical standard state). However, when the equilibrium is not with pure oxygen but with air at 25 ºC and 100 kPa, previous values have to be multiplied by $x_{O2,air}$=0.21, giving 22·0.21=4.6 ppm, 39·0.21=8.2 mg/L, equal to 8.2 mg/kg for water, and equal to 1.2·0.21=0.26 mol/m^3. Finally, the volumetric fractions refer to the volume at 0 ºC and 100 kPa that the full out-gassing of dissolved oxygen in one litre of solution at a given temperature, would occupy: 55 mL/L means that the oxygen dissolved in 1 L of solution would occupy 55 mL as a pure gas at 0 ºC and 100 kPa, a value that is correct for a solution at 25 ºC saturated against pure oxygen at 0 ºC and 100 kPa; if it were against air instead of pure oxygen, the value would be 55·0.21=11.6 mL/L for air at 0 ºC, and, as solubility of gases decreases with temperature and nearly halve from 0 ºC to 25 ºC, in equilibrium with air at 25 ºC and 100 kPa the value is 5.9 mL/L for air at 25 ºC).

We assume a single solute, *s* (of molar mass M_s) dissolved in a solvent, *dis* (of molar mass M_{dis}), but the generalisation to multiple solutes is trivial. Composition may be quantified by the ratio of solute to solution (e.g. moles of solute per litre of solution, grams of solute per kilogram of solution), or by the ratio of solute to solvent, but the former ratio will be favoured here, except in the case is molalities (commonly used to express salt solubilities, however).

A possible grouping for solution quantification may be:

- Moles-of-solute variables.
- Mass-of-solute variables.

- Volume-of-solute variables.

WARNING. In the study of solutions, the litre, L (sometimes with a less distinguishable lower case l), is often used as volume-unit instead of the cubic meter (1 L ≡ 1 dm^3), and the millilitre, mL, is also found in common usage, instead of the cubic centimetre (1 mL≡ 1 cm^3).

Moles-of-solute variables

- Molar fraction of solute, x_s, i.e. moles of solute per mole of solution, either per-one, percent (%) or per million (ppm). Its definition, and relation with other variables, is:

$$x_s \equiv \frac{n_s}{n_s+n_{dis}} = \frac{\dfrac{m_s}{M_s}}{\dfrac{m_s}{M_s}+\dfrac{m_{dis}}{M_{dis}}} = \frac{1}{1+\dfrac{1}{y_s}\dfrac{M_s}{M_{dis}}} = c_s\frac{M_m}{\rho_m} \qquad (5)$$

  where M_m is the molar mass of the mixture, $M_m=x_sM_s+x_{dis}M_{dis}$. For instance, when adding a 10 g bag of sugar ($C_{12}H_{22}O_{11}$) to a 100 cm^3 cup of boiling water (96 g of water, y_x=10/(10+96)=9.4% by weight, having taken 958 kg/m^3 for boiling water), one gets a solution with 0.010/0.342=0.030 moles of sucrose and $958\cdot100\cdot10^{-6}/0.018=5.3$ moles of water, i.e. x_s=0.03/(0.03+5.3)=0.56%, and a concentration of 0.3 mol/L.

  A problem with the amount of substance is that it is not conserved in electrolytic solutions; e.g. seawater with 35 g/kg of NaCl has a molar fraction of dissolved particles of x_s=0.022, mainly sodium cations and chlorine anions; i.e. 1% of the particles are Na^+, 1% are Cl^-, and the rest mainly water molecules; lab seawater may be prepared by adding 0.035 kg of NaCl (0.6 mol) to 1 kg of H_2O (55 mol).
- Molar ratio, $r_s \equiv n_s/n_{dis}$, i.e. moles of solute per mole of solvent; rarely used.
- Molar density, or concentration, c_s, (sometimes written as [formula of solute], e.g. c_{N_2}≡[N_2]) i.e. moles of solute per cubic meter of solution;

$$c_s \equiv \frac{n_s}{V_m} = \frac{x_s n_m}{m_m/\rho_m} = x_s\frac{\rho_m}{M_m} = \frac{m_s/M_s}{V_m} = \frac{\rho_s}{M_s} \qquad (6)$$

  e.g. seawater with 3.5%wt NaCl has a molar density of 600 moles of Na^+ per cubic meter of solution 0.6 mol/L of Na^+), and the sugar solution mentioned above (10 g sucrose in 100 cm^3 of boiling water) has a concentration of $0.03/106\cdot10^{-6}$=28 mol/m^3 (0.28 mol/L, where the fact that adding 10 g sucrose increases 6.5 cm^3 the volume of solution has been used). The problem with molar density is that it changes with temperature even if the system is closed (due to overall volume change).

  Molarity, is just the common way to express molar density, c_s, but taking as unit 1 mol/L instead of 1 mol/m^3, and given it a special, not recommended, symbol: 1 M ≡ 1 mol/L e.g. seawater with 3.5%wt NaCl has approximately 0.6 mol of NaCl per litre of aqueous solution (referred too as 0.6 M NaCl solution (but notice that it is actually a 1.2 mol/L solution since each mole of NaCl yields two moles in solution), and the sugar solution mentioned above is a 0.28 M sucrose aqueous solution (0.28 mol/L solution). WARNING. Some authors use M as the symbol for the mole, instead of the SI-recommended 'mol', and thus write e.g. that seawater is a 0.6 M/L solution, further contributing to the already wide confusion in nomenclature.

Normality, is the mole-equivalent amount of solute (moles divided by valence or replaceable H atoms) per litre of solution; i.e., a normalised molar density, c_s. Often, a special symbol, not recommended, is used for normality: 1 N ≡ 1 mol/L e.g., since NaCl has valence equal to 1, seawater is approximately a 0.6 N Na^+ and 0.6 N Cl^- water solution (in this case 1 N is also 1 M). Normality of a closed system changes with temperature as molarity (molar density) does.

- Molality, b_s, is the amount of solute per mass of solvent, not of solution. Molality is an easy way to specify recipes (the ingredients, instead of the final result), and does not change with temperature in a closed system. Molality is not a recommended composition descriptor; sometimes m is used as symbol for the molality variable, and, to add confusion, sometimes 'm' is used as a molality unit, 1 m ≡ 1 mol/kg; e.g. seawater with 3.5%wt NaCl is approximately a 0.6 m (pronounced 0.6 molal) NaCl solution in water, i.e. adding 0.6 mol of NaCl to one kilogramme of water produces lab seawater. Notice that, although sometimes molality is expressed in mol/L, it is a liberty for the case of water where 1 kg roughly occupies 1 L, but molality is always based on mass of the solvent and does not change with temperature; furthermore, for dilute aqueous solutions, molality values in mol/L (of solvent), practically coincide with molarity values in mol/L (of solution).

$$b_s \equiv \frac{n_s}{m_{dis}} = \frac{n_s}{\rho_{dis} V_{dis}} = \frac{m_s / M_s}{m_{dis}} = \frac{w_s}{M_s} \tag{7}$$

Mass-of-solute variables

Mass-of-solute (or weight) variables have the advantage over molar quantities in that the molecular structure has not to be known; e.g. how many moles are there in one litre of gasoline?):

- Mass fraction of solute, y_s, i.e. kilograms of solute per kilogram of solution, either per-one, percent (%) or per million (ppm); e.g. seawater has a 3.5% mass fraction of dissolved salts (the majority NaCl). WARNING. The recommended symbol under SI-conventions for the mass fraction is w instead of y (but we use w for mass ratio, here).

$$y_s \equiv \frac{m_s}{m_m} = \frac{m_s}{m_{dis} + m_s} = \frac{x_s M_s}{x_{dis} M_{dis} + x_s M_s} \tag{8}$$

- Mass ratio, w_s, usually in units of grams of solute per kilogramme of solvent (absolute humidity is such a mass-ratio function, widely used in Humid air). It is directly related to molality.

$$w_s \equiv \frac{m_s}{m_{dis}} = \frac{n_s M_s}{m_{dis}} = b_s M_s = \frac{m_s}{m_{dis} + m_s - m_s} = \frac{y_s}{1 - y_s} \tag{9}$$

- Solute density in the solution, ρ_s, or mass concentration, usually in units of grams per litre of solution, g/L (many times in mg/L, and the most times in Pharmacy and Medicine in mg/dL (milligrams per decilitre of solution).

$$\rho_s \equiv \frac{m_s}{V_m} = y_s\rho_m = c_s M_s = x_s\rho_m \frac{M_s}{M_m} \qquad (10)$$

- Mass of solute per unit volume of solvent, e.g. in grams of solute per decilitre of solvent (e.g. g/dL means now milligrams per decilitre of solvent), used sometimes to specify solubility data for solids. It can be easily converted to mass ratio by knowing the density of the solvent, ρ_{dis}, by (9).

$$\frac{m_s}{V_{dis}} = \frac{m_s}{m_{dis}/\rho_{dis}} = w_s\rho_{dis} = c_s M_s \rho_{dis} \qquad (11)$$

Volume-of-solute variables

- Volume fraction, v_f, or volume percent (the unit usually being mL/L, or %vol, or % (v/v)), is the volume of pure solute added divided by the sum of solute and solvent volumes before mixing (or after separation, i.e. not by the volume of the solution prepared, although the difference may be negligible for dilute solutions of condensed solutes); i.e. it refers to the recipe to prepare the solution, not to what is obtained. Volume percent, or sometimes volume per volume, is often used when the solute is liquid itself; e.g. ethanol 96% means an aqueous solution that, when separated, corresponds to 96 volumes of ethanol and 4 volumes of water; e.g. a 12% ethanol in water (v/v) solution of 1 L is obtained by mixing 120 cm^3 pure ethanol with 880 cm^3 pure water.

$$v_f \equiv \frac{V_s}{V_m + V_{dis}} = \frac{1}{1+\dfrac{\rho_s/\rho_{dis}}{m_s/m_{dis}}} = \frac{1}{1+\dfrac{\rho_s}{\rho_{dis}}\left(\dfrac{1}{y_s}-1\right)} = \frac{1}{1+\dfrac{\rho_s}{\rho_{dis}}\dfrac{M_{dis}}{M_s}\left(\dfrac{1}{x_s}-1\right)} \qquad (12)$$

- Notice however that there are occasions were the inverse volume fraction is used.
  Volume ratio, v_r, also named Bunsen solubility coefficient, is the volume of pure solute divided by the solvent volumes before mixing (or after separation, i.e. not by the volume of the solution prepared, although the difference may be negligible); i.e. it refers to the recipe to prepare the solution, not to what is obtained. Notice however that there are occasions were the inverse volume fraction is used, as when saying that oxygenated water has 10 volumes of H_2O per one of H_2O_2. For solid and liquid solutes forming dilute solutions, volume ratio and volume fraction practically coincide since $V_{s,\text{pure}} << V_{\text{dis}}$. For gas solutes, the volume the solute would occupy when pure is traditionally measured at the standard temperature and pressure of 0 ºC and 100 kPa: e.g. saying that a soda water has 3 volumes of CO_2 per volume of water, means that there are 132 mol of CO_2 per cubic metre of solution, since a gas at 0 ºC and 100 kPa occupies 44.1 mol/m^3 (3·44=132) When saying that dissolved oxygen in air-saturated water has a concentration of 6 mL/L, one means that there are 6/22.4=0.26 mol/m^3, or 0.008 kg/m^3 of dissolved oxygen.

When specifying concentrations in dimensional units, temperature must be specified also if it affects densities, and, if gases are involved, pressure too must be specified.

Concentration measurement

The experimental finding of qualitative or quantitative composition in a mixture is known as chemical analysis, or simply analysis. We focus here on concentration analysis, assuming the substances involved are already known.

Most methods of concentration analysis are based on measuring solution density (provided the density dependence on solute concentration, $\rho_m=\rho_m(T,p,x_i)$, is known beforehand by calibration), by one of the different techniques:

- Gravimetry. Weighting a known volume of liquid. This is perhaps the easiest and quickest method to measure solution concentration, but requires sampling (e.g. milk producers are paid according to milk density).
- Refractometry. By ray tracing on a sample or in a process flow. Refractive index varies almost linearly with density. This is the easiest way for well-known solutions.
- Resonant vibration. The natural frequency of an encapsulated liquid sample precisely metered depends on its mass. May be applied to a liquid flowing along a bend in a pipe (see Coriolis flowmeter).
- Sonic velocimetry. Density is obtained from $\rho=E/c^2$, where E is the bulk modulus of the solution and c the sound speed through it (see Ultrasonic flowmeter).
- Electric conductivity. This is the best method for very low concentration of electrolytic solutions (e.g. the preferred method for salt-water solutions). The measuring electrodes may be generic, or selective for some specific ion (e.g. Ca^{2+}, NH_4^+, Cl^-, NO_3^-).

Solution preparation from pure solutes and concentrated solutions. Dilution

Solutions can be prepared by simple dilution, either from pure solutes, or from concentrated solutions. Preparing solutions based on molality specifications (you say dissolving with, e.g. dissolving 300 g of NaCl with 1 kg of water) is easy: just measure, add and stir, whereas preparing solutions based on molarity specifications (you say dissolving in), is not so easy: you start with less that a litre of water, then add the solute, stir and keep adding water until a full litre of solution is obtained. To make it more clear, it is difficult to dissolve 300 g of NaCl with 1 kg of water, but it is impossible to dissolve 300 g of NaCl in 1 kg of water solution, since the solubility limit at 15 ºC is 26.4% by weight of NaCl in solution, or 360 g of NaCl with 1 kg of solvent).

Maintaining pure solutes may be tricky, particularly if they are readily oxidised, or hygroscopic, or very volatile or even gaseous. Many salts and hydroxides (e.g. NaOH(s)) are hygroscopic, and will absorb enough water from the air to change its apparent mass if left exposed to the air for long.

Many times, a desired solution is not prepared with the pure solute but from a more concentrated solution (to do it from a more diluted solution you might let some solvent to evaporate, but this is not practical). The basic rule to remember is that adding a concentrated solution to pure solvent maintains the amount of solute, thus $n_s=c_sV_m=c_{s,final}V_{m,final}=c_{s,initial}V_{m,initial}$, from where the appropriate amount of concentrated solution needed, $V_{m,initial}$, may be found.

A basic precaution for the preparation of well-defined aqueous solutions is to use distillated water, instead of tap water, and keep the solution in a closed container.

Dissolving rate

Dissolving takes time, since it only takes place at the interface solute/solvent, driven by the chemical potential difference of the solving species *i*, i.e. to the forcing gradient $\nabla\mu_i$. The dissolving of a solid solute into a liquid solvent is driven by the solvent-molecules pulling out solute-molecules at the surface of the solid and surrounding them in a cluster of solvent-molecules (solvation). Solution equilibrium can be viewed as balanced state where dissolving rate equals segregation rate (crystallization rate, outgassing rate).

Dissolving rate is always proportional to interface area *A*, and it usually increased by stirring or shaking, and by heating, but that only applies to solid solutes; Table 1 summarises the effect of different action on dissolving rate.

Table 1. Effect of different action on dissolving rate.

Action	Dissolving rate of a solid solute	Dissolving rate of a gaseous solute
stirring	increases ($A\uparrow$)	decreases
temperature increase	increases ($\nabla\mu_i\uparrow$)	decreases
pressure increase	has no effect	increases proportionally
crumbling	increases ($A\uparrow$)	Not applicable

The effect of temperature on dissolving rates of solid solutes can be modelled by an Arrhenius law, so that the plot of the logarithm of the time to dissolve a certain amount (in [s]), versus the inverse of temperature, $1/T$ (in [K]), is a straight line of slope $-E_a/R_u$, what yields the dissolving activation energy, E_a (in [J/mol]), after multiplication by R_u=8.3 J/(mol·K).

Electrolytic solutions

When a solute dissolves in a liquid, its molecules always get apart from each other to be surrounded by solvent molecules (that is ‘to dissolve’), but sometimes solute molecules get split into ions, yielding an electrolytic solution, also known as ionic solution or simply an electrolyte. Most electrolytic solutions come from ionic solutes (e.g. NaCl), but there are molecular solutes that yield electrolytic solutions (e.g. HCl(g), NH_3(g)).

An electrolyte is a volumetric ionic system; i.e. a system that transport electricity in relatively slow-moving particles (ions, from Gr. *ienai* to go) instead of by rapid moving electrons in a solid conductor. Electrolytes can be solid (like the polymer membranes used in PEM-fuel-cells or the oxides used in SO-fuel-cells), or they can be liquid (either a high-temperature melt like NaCl above 804 ºC, or a room-temperature solution in a given solvent, like NaCl(aq); we here deal only with the latter). Water is the most important solvent for electrolytes (ethanol, ammonia, and acetic acid are some of the non-aqueous solvents that are able to dissolve electrolytes). Electrolytes are electrically neutral, i.e. they have the same number of positive and negative charges. Electric conduction within an electrolyte implies electrochemical reactions at some charge-balancing electrodes (i.e. a closed electrical circuit).

Solution electrolytes may be salts, acids or bases; e.g. NaCl(aq), HCl(aq) and NaOH(aq). Weak electrolytes partially dissociate (e.g. acetic acid and ammonia; acetic acid 0.001 M only dissociate up to 12% in water at 25 ºC), whereas strong electrolytes dissociate almost completely (e.g. NaCl(s), HCl(g), NaOH(s), H_2SO_4(l); NaCl(s) dissociate more than 99%). All electrolytes dissociate to some degree, but when the dissociation is very large they are called strong electrolytes (i.e. the proportion of solute molecules to ions is negligible). At small concentrations, the electrical conductivity of electrolytes is proportional to ion concentration.

When a ionic compound dissolves, ions get free from their partners, but get surrounded by the polar molecules of the solvent, an arrangement that has always less energy than the isolated ion, what implies there is a positive solvation energy (hydration energy for water solutions).

Solution properties

To begin with, notice that ,although most properties are associated to the solute, and so labelled (e.g. the solubility of common salt is 26%wt in solution), and some other properties just to the solvent (e.g. freezing-point depression), all solution properties depend to some extent on the solute considered, the solvent, other solutes present, concentrations, temperature and pressure.

One of the key properties of a solution is solubility, i.e. how much solute the solvent can dissolve, best seen on a phase diagram, although phase diagrams are usually quite complex and just a table of solubilities, or at most a solubility-vs-temperature curve, is presented.

Besides the phase diagram for the mixture (or just vapour-liquid equilibrium data (VLE), or a simple solubility limit at room temperature), other properties of solutions are of interest, here grouped as:

- Solubility dependence with temperature, and other phase-diagram related data, as melting point, boiling point, vapour pressure, formation of compounds (e.g. hydrate, clathrate), etc.
- Density dependence on solute concentration. This is usually the basic measure in solutions.
- Heat of solution. This is only important for large-size industrial systems, or when the application is based on that (as for freezing mixtures), or when, jointly with entropy of mixing, properties are to be deduced from thermochemical data (see Solute equilibrium, below).
- Other properties: thermal capacity, thermal conductivity, viscosity, diffusivity, refractive index, electrical conductivity, etc.

Phase diagram

Solutions, as for general mixtures, are homogeneous systems (more or less stratified in the presence of a force field), that may be in contact with other phases, forming multiphase systems. While phase diagrams for pure components are presented as p-T diagrams (see Potentials and properties), phase diagram for a mixture, are usually based on a T-x diagram (temperature versus concentration, at ambient pressure), where one may see at a glance the main thermodynamic characteristics of the system: solubility, melting and boiling points, and their temperature dependence.

There are functions that may be deduced from the phase diagram, as the enthalpy of solution (related to solubility dependence on temperature), but some others are usually plotted aside, like density variation with concentration. Phase diagrams for ideal binary mixtures have been presented aside (see Mixtures), but they only apply to liquid-vapour equilibrium of similar components; most solutions deviate a lot from ideal mixtures, and their phase diagram has little resemblance; see Fig. 1 for some examples.

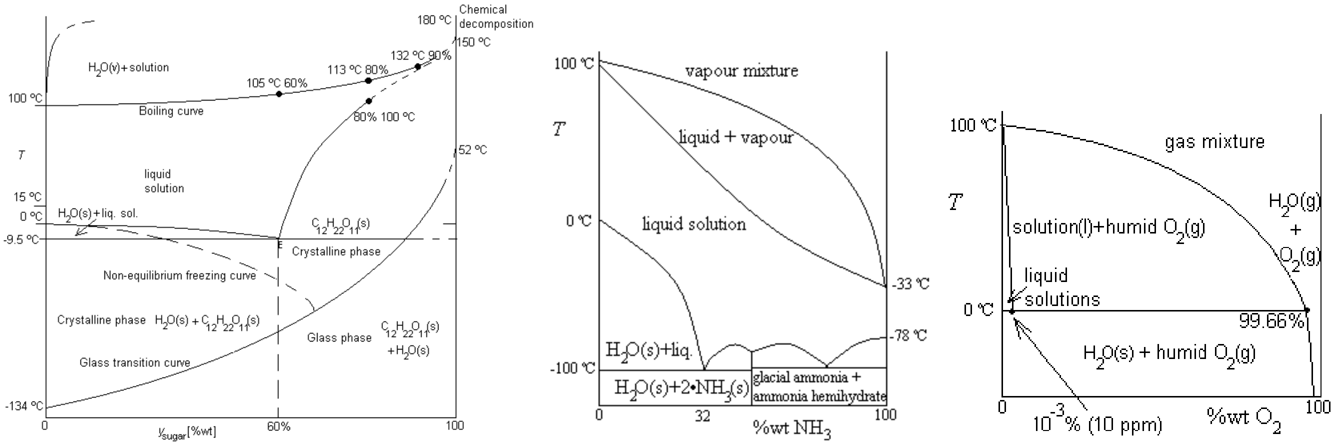

Fig. 1. Phase diagram for some binary mixtures: a) a solid solute: sucrose-water solutions, b) a liquid solute: ammonia-water solutions, c) a gas solute: oxygen-water solutions.

Notice that phase diagrams present equilibrium states, although in some rare occasions they also include some metastable states, as the glass states in Fig. 1a.

Contrary to the monotonic behaviour of the boiling and condensation lines in ideal mixtures, the boiling line in non-ideal mixtures may have a relative maximum or minimum. 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 ºC while $T_{b,water}$=100 ºC and $T_{b,nitric}$=87 ºC), 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 ºC while $T_{b,water}$=100 ºC and $T_{b,ethanol}$=78.4 ºC).

Non-ideal mixtures usually present one or more minima in the liquidus line (freezing point), called eutectic points (the easier to melt)., below which the homogeneous liquid solution segregates into an heterogeneous solid mixture with two different compositions. Typical eutectics are T_{eu}=–21 ºC for water (T_f=0 ºC) and common salt (T_f=801 ºC) with y_{NaCl}=0.23, T_{eu}=183 ºC for tin (T_f=232 ºC) and lead (T_f=327.5 ºC) with y_{Pb}=0.33, T_{eu}=578 ºC for aluminium (T_f=657 ºC) and silicon (T_f=1412 ºC) with y_{Si}=0.11 and T_{eu}=1130 ºC for iron (T_f=1539 ºC) and carbon (T_f=3530 ºC) with y_C=0.043.

The focal point on a solution-phase-diagram is the liquid solution region (or regions, if immiscible liquids), horizontally-limited by a possible liquid-liquid equilibrium, LLE, and vertically-limited upwards by the vapour-liquid-equilibrium, VLE, and downwards by the solid-liquid-equilibrium SLE.

Thermodynamics of solubility

Solubility is a quantitative measure of the maximum amount of solute (gas, liquid, or solid) that can be dissolved in a given solvent (pure component or mixture, liquid or solid), i.e. the equilibrium composition of a saturated solution. Solubility is a thermodynamic function that depends on the substances (solute and solvent), temperature and pressure; if more solute is present it will form a separate phase (pure solid, a hydrate compound, another liquid phase or a gas phase).

A solution is called saturated if it contains the maximum dissolvable amount. Solutions may be unsaturated (solute concentration below its solubility limit), at equilibrium (solubility concentration), or supersaturated (a metastable state that will settled after a while if disturbed).

Hydrophobic effect

It is the tendency of nonpolar substances to aggregate in an aqueous solution and exclude water molecules due to the entropy change of water surrounding nonpolar solute molecules. If one considers the Gibbs energy change, $\Delta G=\Delta H-T\Delta S$, between a real immiscible oil-water mixture, and its imaginary perfectly mixed configuration, the enthalpy change cannot be large (one may even think of an oil with the same density of water), hence, the tendency to demix must be due to an entropic effect. However, for the oil molecules, the tendency is to get dispersed. The explanation comes from the entropy change in water: to hold the dispersed nonpolar molecules, the polar water molecules must rearrange to maximize the number of H-bonds they make with one another, forming an ordered ‘cage’ as in ice; therefore, it is the tendency of H-bonded water molecules to remain disordered what (randomly) kicks the nonpolar molecules out of the solution. The hydrophobic effect is essential in biology, particularly for cell membrane functions and macromolecules’ folding.

Qualitative solubility. Solubility rules

Although all solutes dissolve more or less in all solvents, there are great differences between different couples, and, in qualitative terms, the following classification is applied to a given solute with respect to a given solvent at ambient temperature:

- Insoluble, if the solvent barely can hold any amount of solute (say $c_s<0.01$ mol/L; e.g. $CaCO_3$ is said to be insoluble in water). Carbonates, oxides, some sulfates (Ca, Ba), and most gases can be considered insoluble in water (but recall that fish breath just from the tiny amount of oxygen dissolved).
- Slightly soluble, say in the range 0.01 mol/L$<c_s<0.1$ mol/L (e.g. $Ca(HCO_3)_2$ in water, $CO_2(g)$ in water).
- Soluble, if the solvent can hold a large amount of solute but up to a limit (say >0.1 mol/L, e.g. NaCl in water up to 5.6 mol/L). All sodium, potassium and ammonium salts are soluble in water, as well as all nitrates, acetates, perchlorates, chlorides, bromides and iodides. All alkaline hydroxides, and barium hydroxide, are soluble in water.
- Miscible, if solute and solvent can mix in any proportion (e.g. ethanol in water).

The basic rule for miscibility is: 'likes dissolve likes' (e.g. polar liquids like water dissolve polar liquids like alcohols, ammonia, acids and alkalis, whereas non-polar liquids like benzene dissolve non-polar liquids like hydrocarbons).

Solute equilibrium and its temperature variation

Solubility, being a two-phase equilibrium, depends on temperature, pressure and the presence of other solutes. The chemical potential of each component must be uniform at equilibrium, so that for the equilibrium of a solute 's' between the liquid solution 'liq' and its pure phase (here assumed to be a solid phase 'sol', but also valid for any other phase), in the ideal limit, verifies:

$$\mu_{s,liq}(T,p,x_{s,liq})=\mu_{s,sol}(T,p,x_{s,sol}) \quad \longrightarrow \mu^{\infty}_{s,liq}(T,p)+RT\ln x_{s,liq}=\mu^{*}_{s,sol}(T,p)$$

$$\ln x_{s,liq}=\frac{-\left(\mu^{*}_{s,sol}(T,p)-\mu^{\infty}_{s,liq}(T,p)\right)}{RT}=\frac{-g_{s,sol-liq}(T,p)}{RT}=\frac{-h_{s,sol-liq}(T,p)}{RT}+\frac{s_{s,sol-liq}(T,p)}{R} \quad (13)$$

i.e., the solubility $x_{s,liq}$ (or simply x_s) can be obtained from the solution-enthalpy and solution-entropy changes, tabulated as Thermochemical data of solutes.

Neglecting the variations of the enthalpy and entropy changes with temperature, the variation of solubility with temperature within this ideal model would be (van't Hoff equation):

$$\frac{d\ln x_{s,liq}}{d\dfrac{1}{T}}=\frac{-h_{s,sol-liq}(T,p)}{R} \qquad (14)$$

and, the right-hand-side being small and its variation with temperature even smaller, one may conclude that:

- Solubilities can be obtained from Thermochemical data of solutes in the dissolving process, which is treated as a 'reaction'. The standard state for solutes in those tabulations is the infinite-dilute solution extrapolated to a concentration $c_{i,liq,Ref}$=1 mol/L of solution (1 molar); notice that another reference state is sometimes used: the 1 mol/kg of solvent (1 molal).
- Solubility changes with temperature according to the value of the heat of solution: solid solutes usually give way to endothermic mixing and thus solubility increases with temperature, whereas gas solutes give way to exothermic mixing and thus solubility decreases with temperature (see Solubility data for aqueous solutions).
- The solubility curve as a function of 1/*T* should be a straight line of small slope (in spite of this advantage, most graphs use *T* as variable, instead of 1/*T*).

Solubility data are commonly tabulated explicitly in terms of saturation concentration (see Solubility data for aqueous solutions), either per volume of solution (maximum achievable concentration), or per volume of solvent (molality), or per mass of solvent (mass ratio), or implicitly in terms of the equilibrium constant for the dissolving process, or related thermochemical data as in Thermochemical data of solutes. For instance, common-salt in water at 15 ºC has a solubility of y_s=0.264%wt (meaning e.g. that no more than 264 g of NaCl(s) can be dissolved in 736 g of H_2O(l)), equivalent to a solubility of 0.356 kg of NaCl(s) per 1 kg of H_2O(l), equivalent to a solubility of 4.7 molal solution (meaning that no more than 4.7 mol of NaCl(s), M=0.058 kg/mol, can be dissolved in 1 kg of H_2O(l)), equivalent to a solubility of 5.6 molar solution (meaning that no more than 5.6 mol of NaCl(s) can be dissolved in 1 litre of brine), equivalent to a solubility-product constant K_{sp}=5.6^2=31 (mol/L)^2, equivalent to a standard Gibbs-function change upon solution of $\Delta G=-RT\ln K_{sp}=-8.5$ kJ/mol.

Exercise 1. Solubilities from thermochemical data

Solubility equilibrium for gas solutes

There are several examples of natural solutions of gases in liquids, perhaps the most important being the solution of oxygen from ambient air in fresh water and seawater, what allows for the breathing of all fish (sea-mammals breath from atmospheric air) and submerged flora; other examples of gas solutes being natural-carbonated spring-water sources, and putrid waters holding hydrogen sulphide. It is worth insisting on the fact that true solutions are single homogeneous phases; e.g. a carbonated drink has no bubbles within, at equilibrium; bubbles appear when pressure is released and the solution is not at equilibrium.

Solubility of pure gases in liquids is proportional to pressure, due to the great density change on condensation ($\Delta s<0$ for gas→solution), but most gases become less soluble as the temperature increases, implying they have negative enthalpy of solution ($\Delta h<0$ for gas→solution, i.e. exothermic mixing, see Thermochemical data of solutes). On the contrary, with few exceptions, the solubility of solids and liquids in another liquid increases with temperature (i.e. endothermic mixing), and the effect of pressure is negligible. Notice, by the way, that in real experiments, one cannot have a pure gas in equilibrium with its water solution because there would be some water-vapour dissolved in the gas (e.g. for oxygen and water at 100 kPa and 25 ºC, there is some 3.17% of vapour in the gas).

Care must be paid to the standard condition assumed, otherwise it might be puzzling to analyse the spontaneity of a reaction like $CO_2(g)\to CO_2(aq)$, which at standard conditions is (from Thermochemical data of solutes), $\Delta G=-386-(-394)=8$ kJ/mol; it does not mean that carbon dioxide cannot dissolve in water at the standard conditions of 298 K and 100 kPa; it really means that if, under this conditions, pure $CO_2(g)$ were put in contact with an ideal aqueous solution containing 1 mol/L (the standard concentration) of $CO_2(aq)$, the natural tendency would be not to dissolve further but to degas until the equilibrium is reached (standard solubility is just 0.032 mol/L=1.5 g/L, after Solubility data for aqueous solutions).

For an ideal binary liquid-vapour mixture at equilibrium, the molar fraction in the liquid phase at equilibrium can be obtained from Raoult's law (1), but this ideal model only applies to very similar components: propane-butane mixtures, benzene-toluene, nitrogen-oxygen at cryogenic temperatures, and with less accuracy to water-H_2O_2 mixtures, water-methanol or water-ammonia. Most gas solutions of interest require an empirical modification of Raoult's law proposed by W. Henry in 1803 for the solubility of non-dissociating gases in liquids:

$$\frac{x_{i,gas}}{x_{i,liq}}=\frac{k_{i,liq}(T)}{p} \qquad (15)$$

where $k_{i,liq}(T)$ is assumed to be independent of pressure and is named Henry's constant (depends on temperature, tending to zero as the boiling point of the solvent is approached, and on the solvent). Notice that, by (15), solubility of a gas is proportional to applied pressure (this is valid for not too-high pressure). As for ideal mixtures, the product of molar fraction times pressure, $x_{i,gas}p$, appears so often in gases, that a new variable is defined, named partial pressure, $p_i \equiv x_{i,gas}p$ (as if actual pressure was due to the sum of partial pressures from each component). Henry's equation (15) can be deduced similarly to Raoult equation (1):

$$\mu_{s,liq}(T,p,x_{s,liq}) = \mu_{s,gas}(T,p,x_{s,gas}) \quad \longrightarrow \mu^{\infty}_{s,liq}(T,p) + RT\ln x_{s,liq} = \mu^{*}_{s,gas}(T) + RT\ln\left(\frac{x_{s,gas}p}{p^{\oplus}}\right)$$

$$\ln\frac{x_{s,liq}}{x_{s,gas}p/p^{\oplus}} = \frac{-\left(\mu^{\oplus}_{s,gas}(T) - \mu^{\infty}_{s,liq}(T)\right)}{RT} = \frac{-g^{\oplus}_{s,gas-liq}(T)}{RT} \qquad (16)$$

with the last right-hand-side being just a function of T that allows a rearrangement like (15). Besides the constant $k_{i,liq}$ in (15), several other related forms of Henry law constant are commonly used, defined and related to each other as follows (we named with small case k those forms similar to (15), with two super-indices indicating the variables divided, and with capital K their inverses):

$$\left.\begin{array}{l}
\underset{K^{cc}_{i,liq}(T)}{\frac{c_{i,liq}}{c_{i,gas}}} = \underset{K^{cp}_{i,liq}(T)}{\frac{c_{i,liq}}{p_{i,gas}}} R_uT = \underset{K^{\rho p}_{i,liq}(T)}{\frac{\rho_{i,liq}}{p_{i,gas}}} \frac{R_uT}{M_i} = \underset{K^{xp}_{i,liq}(T)}{\frac{x_{i,liq}}{p_{i,gas}}} \frac{\rho_m R_uT}{M_m} = \underset{K^{xx}_{i,liq}(p,T)}{\frac{x_{i,liq}}{x_{i,gas}}} \frac{\rho_m R_uT}{pM_m} \\
\underset{k^{cc}_{i,liq}(T)}{\frac{c_{i,gas}}{c_{i,liq}}} = \underset{k^{pc}_{i,liq}(T)}{\frac{p_{i,gas}}{c_{i,liq}}} \frac{1}{R_uT} = \underbrace{\frac{p_{i,gas}}{\rho_{i,liq}} \frac{M_i}{R_uT}}_{k^{p\rho}_{i,liq}(T)} = \underbrace{\frac{p_{i,gas}}{x_{i,liq}} \frac{M_m}{\rho_m R_uT}}_{k^{px}_{i,liq}(T)} = \underbrace{\frac{x_{i,gas}}{x_{i,liq}} \frac{pM_m}{\rho_m R_uT}}_{k^{xx}_{i,liq}(p,T)}
\end{array}\right\} \qquad (17)$$

Perhaps the most rational approach to present gas-solubility data is by means of $K^{cc}_{i,liq}(T)$, as advocated by Ostwald (it is the only non-dimensional choice of 'Henry-constant', all others being dimensional or depending on pressure), indicating the quotient between the amount of gas dissolved per unit volume of liquid, and the amount of gas per unit volume of gaseous phase, and some values are presented in Solubility data for aqueous solutions. Inverse constants really refer to volatility instead of solubility. The traditional way, however, to present solubility data, is in terms of K^{cp}, and the relations among them and with the Gibbs function of solution, from (16), is:

$$K^{cc}(T) = K^{cp}(T)R_uT = K^{\rho p}(T)\frac{R_uT}{M_i} = K^{xp}(T)\frac{\rho_m R_uT}{M_m} = K^{xx}_{i,liq}(p,T)\frac{\rho_m R_uT}{pM_m} = \frac{c^{\oplus}R_uT}{p^{\oplus}}e^{\frac{-g^{\oplus}_r(T)}{R_uT}} \qquad (18)$$

where, R_u=8.3 J/(mol·K) and the constants traditionally used are $p^{\oplus}$=100 kPa (1 bar), $c^{\oplus}$=1 mol/L (1 molar). For dilute aqueous solutions, ρ_m=1000 kg/m^3 and M_m=0.018 kg/mol.

Exercise 2. Thermochemical data from solubilities

As a check for gas-solubility data-consistency, the particular data for the equilibrium of pure oxygen (M_i=0.032 kg/mol) with pure water, when the two-phase mixture attains equilibrium at 25 ºC and 100 kPa (we take for the mixture properties M_m=0.018 kg/mol and ρ_m=1000 kg/m^3), is presented below in all the above forms.

$$\left.\begin{array}{l}
\underset{K^{cc}_{i,liq}(T)=0.032}{\frac{c_{i,liq}}{c_{i,gas}}} = \underset{K^{cp}_{i,liq}(T)=1.3\frac{\frac{\mathrm{mol}}{\mathrm{m}^3}}{\mathrm{bar}}}{\frac{c_{i,liq}}{p_{i,gas}}} \underset{0.025\,\frac{\mathrm{bar}}{\frac{\mathrm{mol}}{\mathrm{m}^3}}}{R_uT} = \underset{K^{\rho p}_{i,liq}(T)=0.041\frac{\frac{\mathrm{kg}}{\mathrm{m}^3}}{\mathrm{bar}}}{\frac{\rho_{i,liq}}{p_{i,gas}}} \underset{0.77\,\frac{\mathrm{bar}}{\frac{\mathrm{kg}}{\mathrm{m}^3}}}{\frac{R_uT}{M_i}} = \underset{K^{xp}_{i,liq}(T)=23\cdot10^{-6}\frac{1}{\mathrm{bar}}}{\frac{x_{i,liq}}{p_{i,gas}}} \underbrace{\frac{\rho_m R_u T}{M_m}}_{1370\ \mathrm{bar}} = \underbrace{\frac{x_{i,liq}}{x_{i,gas}}}_{K^{xx}_{i,liq}(p,T)=23\cdot10^{-6}} \underbrace{\frac{\rho_m R_u T}{pM_m}}_{1370} \\
\\
\underbrace{\frac{c_{i,gas}}{c_{i,liq}}}_{k^{cc}_{i,liq}(T){}^\wedge=31} = \underbrace{\frac{p_{i,gas}}{c_{i,liq}}}_{k^{pc}_{i,liq}(T)=0.78\frac{\mathrm{bar}}{\frac{\mathrm{mol}}{\mathrm{m}^3}}} \underbrace{\frac{1}{R_uT}}_{40\frac{\frac{\mathrm{mol}}{\mathrm{m}^3}}{\mathrm{bar}}} = \underbrace{\frac{p_{i,gas}}{\rho_{i,liq}}}_{k^{p\rho}_{i,liq}(T)=24\frac{\mathrm{bar}}{\frac{\mathrm{kg}}{\mathrm{m}^3}}} \underbrace{\frac{M_i}{R_uT}}_{1.3\frac{\frac{\mathrm{kg}}{\mathrm{m}^3}}{\mathrm{bar}}} = \underbrace{\frac{p_{i,gas}}{x_{i,liq}}}_{k^{px}_{i,liq}(T)=43\cdot10^3\,\mathrm{bar}} \underbrace{\frac{M_m}{\rho_m R_u T}}_{0.73\cdot10^{-3}\frac{1}{\mathrm{bar}}} = \underbrace{\frac{x_{i,gas}}{x_{i,liq}}}_{k^{xx}_{i,liq}(p,T)=43\cdot10^3} \underbrace{\frac{pM_m}{\rho_m R_u T}}_{0.73\cdot10^{-3}}
\end{array}\right\}(19)$$

with the following interpretation:

- Solubility $K^{cc}_{O_2(g),H_2O(l)}$ =0.032 at 25 ºC means that if there were 1 mol/m^3 of oxygen in a gas phase mixture, there would be 0.032 mol/m^3 of oxygen in the liquid phase mixture.
- Volatility $k^{cc}_{O_2(g),H_2O(l)}$ =31 at 25 ºC means that if there were 1 mol/m^3 of oxygen in a liquid phase mixture, there would be 31 mol/m^3 of oxygen in the gas phase mixture.
- Henry constant of solubility $K^{cp}_{O_2(g),H_2O(l)}$ =13·10^{-6} (mol/m^3)/Pa at 25 ºC means that if there were 100 kPa of oxygen partial pressure in a gas phase mixture, there would be $c_{O_2(g),liq}$ =1.3 mol/m^3 of oxygen in the liquid phase mixture.
- Henry constant of volatility $k^{pc}_{O_2(g),H_2O(l)}$ =0.078·10^6 Pa/(mol/m^3) at 25 ºC means that a partial pressure of 0.078 MPa of oxygen in the gas mixture would create a $c_{O_2(g),liq}$ =1 mol/m^3 oxygen concentration in the liquid mixture..
- Henry constant of solubility $K^{xp}_{O_2(g),H_2O(l)}$ =0.23·10^{-9} Pa^{-1} means that 100 kPa of oxygen partial pressure would produce a $x_{O_2(g),liq}$ =23 ppm molar fraction of oxygen in the liquid phase (i.e. 23 O_2 molecules per million of molecules, the vast majority of them H_2O molecules).
- Henry constant of volatility $k^{px}_{O_2(g),H_2O(l)}$ =4300·10^6 Pa means that 0.43 MPa of oxygen partial pressure would produce a 100 ppm (0.01%) molar fraction of oxygen in the liquid phase.
- Henry constant of solubility $K^{\rho p}_{O_2(g),H_2O(l)}$ =0.41·10^{-6} (kg/m^3)/Pa means that 100 kPa of oxygen in a gas phase mixture would produce $\rho_{O_2(g),liq}$ =0.041 kg/m^3 of oxygen in the liquid phase mixture.
- Henry constant of volatility $k^{p\rho}_{O_2(g),H_2O(l)}$ =2.4·10^6 Pa/(kg/m^3) means that 2.4 MPa of oxygen partial pressure would produce a $\rho_{O_2(g),liq}$ =1 kg/m^3 of oxygen in the liquid phase.
- Henry constant of solubility $K^{xx}_{O_2(g),H_2O(l)}$ =43·10^3 means that 1 ppm-molar of oxygen in the gas phase mixture would produce a molar fraction of $x_{O_2(g),liq}$ =0.043 of oxygen in the gas phase mixture.
- Henry constant of volatility $k^{xx}_{O_2(g),H_2O(l)}$ =23·10^{-6} means that a molar fraction of 1 of oxygen in the gas phase (i.e. pure oxygen) would produce a molar fraction of $x_{O_2(g),liq}$ =23·10^{-6} of oxygen in the liquid phase at standard pressure and temperature.

As a further check, consider water at 25 ºC in equilibrium with air at 100 kPa (oxygen partial pressure is 21 kPa). The equilibrium composition is as follows (Table 2):

- In the gas phase, assuming air to be initially 79% N_2 plus 21% O_2 in volume, there will be a 3-component mixture (N_2, O_2 and H_2O) that to a first approximation has $x_{O_2(g),gas}$ =0.21, or $c_{O_2(g),gas}$ $=x_ip/(R_uT)$=8.5 mol/m^3, or $y_{O_2(g),gas}$ =0.23, or $\rho_{O_2(g),gas}=y_{O_2(g),gas}\rho$=0.23·1.17=0.27 kg/m^3.

- In the liquid phase, there will be also a 3-component mixture (N_2, O_2 and H_2O), but now with the following oxygen concentration (all of them equivalent):

Table 2. Oxygen concentration in water, in equilibrium with air at 25 ºC and 100 kPa.

Value	Comment
$x_{O_2(g),liq}=23\cdot10^{-6}\cdot0.21=4.8\cdot10^{-6}$	i.e. a 4.8 ppm molar fraction of oxygen; from $K^{xp}_{O_2(g),H_2O(l)}=2.3\ Pa^{-1}$
$c_{O_2(g),liq}=1.3\cdot0.21=0.27$ mol/m^3	0.27 mol / (1000 kg / 0.018 kg/mol) = $4.8\cdot10^{-6}$, i.e. consistent
$\rho_{O_2(g),H_2O(l)}=0.041\cdot0.21=0.0086$ kg/m^3	0.0086 kg/m^3 / 0.032 kg/mol = 0.27 mol/m^3, i.e. consistent
$4.3\cdot10^{-6}$ mol/mol=$7.6\cdot10^{-6}$ kg/kg	i.e. there is $y_{O_2(g),liq}=7.6$ mg/kg of dissolved oxygen
5.9 mL/L (STP)	i.e. the 7.6 mg/L in liquid phase at 25 ºC would occupy $7.6\cdot(8.3/0.032)\cdot273/10^5=5.4$ mL/L as pure gas at 0 ºC and 100 kPa

All fish and plants in fresh and salt water breath from dissolved oxygen, that can hardly sustain life if its concentration is below say 4 mg/L (0.004 kg/m^3); actual oxygen concentration on surface waters may vary from 0 to 15 mg/L, depending on the biota decaying and photosynthesis process taking place. Oxygen dissolves less in seawater than in fresh water; at 0 ºC saturation decreases from 14.6 mg/L in pure water to 11.5 mg/L in 35‰ seawater; at 25 ºC saturation decreases from 7.6 mg/L in pure water to 6.1 mg/L in 35‰ seawater

An ambiguous question may be: where there is more oxygen, in the air, or dissolved in water? Assuming the question is understood 'per unit volume', there are 8.5 mol/m^3 of oxygen in the air and 0.27 mol/m^3 of oxygen in air-saturated water; the ratio being $0.27/8.5=0.032=K^{cc}_{O_2(g),H_2O(l)}$; in another way, there are 0.27 kg/m^3 of oxygen in the air and 0.0086 kg/m^3 of oxygen in air-saturated water; the ratio being again $0.0086/0.27=0.032=K^{\rho\rho}_{O_2(g),H_2O(l)}=K^{cc}_{O_2(g),H_2O(l)}$. Nevertheless, because there is 300 times more water-mass in the oceans than air-mass in the atmosphere, assuming that the oxygen concentration in the ocean does not vary too much in depth, there is more mass of air (or amount of air) dissolved in the oceans than in the atmosphere.

Exercise 3. Nitrogen release in sudden decompression

Solubility equilibrium for solid solutes

As said before, two-phase solute/solution equilibrium in a binary mixture (solubility equilibrium for short), can be studied similarly to chemical-reaction equilibrium, and equilibrium composition, $x_{s,liq}$, i.e. the solubility, can be obtained from the solution-enthalpy and solution-entropy changes, tabulated as in Thermochemical data of solutes. It is customary, however to tabulate directly the solubility value at standard conditions, as it can be found for water solutions of solid, liquid or gaseous solutes in Solubility data for aqueous solutions. Fig. 2 presents the temperature dependence of solubility for some solid solutes.

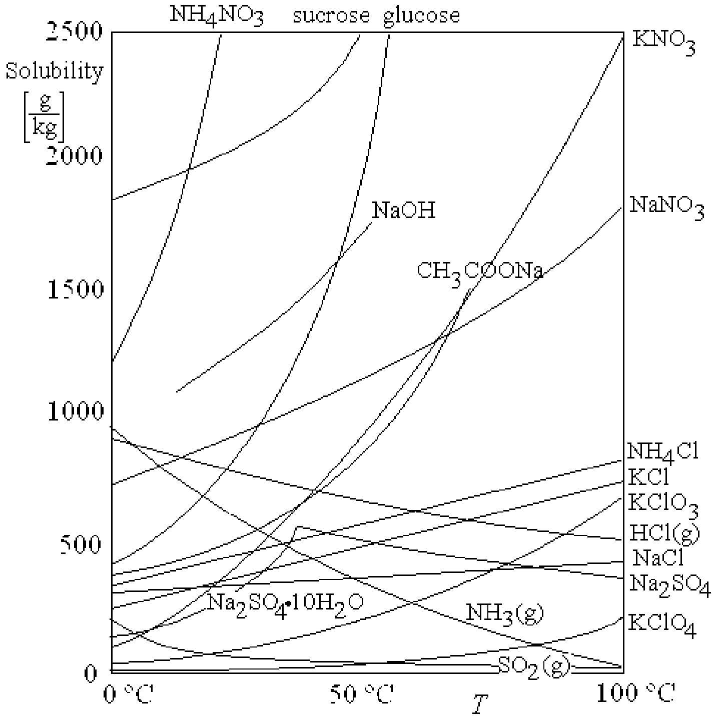

Fig. 2. Solubility limits, in grams of solute per kilogram of solvent (not of solution), versus temperature, for some salts and some soluble gases in water.

For non-electrolytic solutes (also known as molecular solids), a solubility equilibrium constant (dependent on temperature as for chemical equilibrium constants) may be defined such that:

$$K_s \equiv a(\mathrm{A}) \approx [\mathrm{A}] \qquad \text{for a non-electrolytic solution equilibrium A(s)} \rightarrow \text{A(aq)} \qquad (20)$$

For electrolytic solutes (also known as ionic solids), the solubility equilibrium constant, known as solubility-product constant, K_{sp} may be defined such that:

$$K_s \equiv a(\mathrm{A}^+)a(\mathrm{B}^-) \approx [\mathrm{A}^+][\mathrm{B}^-] \quad \text{for an electrolytic solution equilibrium AB(s)} \rightarrow \mathrm{A}^+\text{(aq)}+\mathrm{B}^-\text{(aq)} \quad (21)$$

As before, the approximation of activities, a_i, by concentrations $[M] \equiv c_i$ (i.e. molarities, usually in mol/L of solution, but other times by molalities in mol/kg of solvent) is valid for sparingly soluble salts and gases (better than for acids or bases).

Almost all salts are strong electrolytes, i.e. they dissolve as separate positive and negative ions. Solubility of ionic compounds presents some new characteristics relative to non-electrolytic solutes, namely the common-ion effect and the cross-reaction precipitation. The common-ion effect refers to the effect on solubility of an ion that is already in solution; when a solute AB dissolves in an BC aqueous solution instead of in pure water, the [B] from BC counts in the solubility-product constant, K_{sp}, and thus AB cannot dissolved as much as in pure water. The cross-reaction precipitation refers to the effect of indirect precipitation of a ion by reaction of others, as when calcium ions are removed from hard water (i.e. with high $Ca(HCO_3)_2(aq)$ concentration) by adding $Ca(OH)_2(aq)$ to force the process $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$, with the consequence $Ca(HCO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow 2CaCO_3(s) + H_2O(l)$.

Solubilities may show big changes when the solute is a hydrate, since, when temperature increases, a point might be reached where the hydrate becomes unstable and begins to lose water; e.g. the solubility of $Na_2SO_4\cdot 10H_2O(s)$ increases rapidly with increasing temperature, from 50 g/kg of water at 0 ºC, to 550 g/kg of water at 32.4° C; but above 32.4° C the stable form is $Na_2SO_4(s)$, and its solubility decreases as the temperature increases.

For ions in solution, the hydrated hydrogen ion $H^+(aq)$ is taken as reference for all other aqueous ions, since a solution cannot contain only ions of one kind (bulk phases must be electrically quasi-neutral to not disintegrate). Thermochemical data of solutes in the case of ions is commonly ordered by electropositiveness, i.e. in terms of the reduction potential, i.e. that corresponding to the reduction reaction (that consumes electrons, e.g. $Na^+(aq)+e^-=Na(s)$ or $(1/2)Cl_2(g)+e^-=Cl^-(aq)$), whereas thermochemical data applies to the reaction of formation from the natural elements and may be a reduction or an oxidation reaction. When the formation reaction is a reduction reaction (e.g. $(1/2)Cl_2(g)+e^-=Cl^-(aq)$), $\varepsilon^{\oplus}=-g_f{}^{\oplus}/(zF)$ and $d\varepsilon^{\oplus}/dT=s_f{}^{\oplus}/(zF)$), whereas when the formation reaction is an oxidising reaction ($Na(s)=Na^+(aq)+e^-$), then $\varepsilon^{\oplus}=g_f{}^{\oplus}/(zF)$ and $d\varepsilon^{\oplus}/dT=-s_f{}^{\oplus}/(zF)$). Thence, the Gibbs function for a redox solution reaction as $Na(s)+(1/2)Cl_2(g)=Na^+(aq)+Cl^-(aq)+73$ kJ/mol, is computed as $g_{\rm r}{}^{\oplus}=g_f{}^{\oplus}{}_{\rm f,Cl}+g_f{}^{\oplus}{}_{\rm f,Na+}=-131-262=-392$ kJ/mol, whereas the electrical potential produced by this redox reaction is computed as $\varepsilon^{\oplus}{}_{\rm r}=\varepsilon^{\oplus}{}_{\rm f,Cl-}-\varepsilon^{\oplus}{}_{\rm f,Na+}=1.36-(-2.71)=4.07$ V, or by $\varepsilon^{\oplus}{}_{\rm r}=-g_r{}^{\oplus}/(zF)=-(-392000)/(1\cdot 96500)=4.07$ V.

You may notice that most standard enthalpies for ions are negative, meaning that ion formation within a liquid is an exothermic process, contrary to ion formation in gas phase, as for protons in a gas, $H^+(g)$, that is highly endothermic. Notice also that all the standard entropies (absolute entropies) of molecular solutes are positive (they are monotonous functions of thermal capacities), whereas many ionic solutes show negative standard entropies.

With the traditional choice for the standard state in solutions ($c^{\oplus}=1$ mol/L, ideal 1 molar solution), the relations amongst the different solubility variables for non-ionic solutions are:

$$\ln\frac{c_{s,liq}}{c^{\oplus}}=\frac{-g^{\oplus}_{s,sol-liq}}{RT^{\oplus}}=\frac{-\left(g^{\oplus}_{f,s,aq}-g^{\oplus}_{f,s}\right)}{RT^{\oplus}},\quad \frac{d\ln c_{s,liq}}{d\frac{1}{T}}=\frac{-h^{\oplus}_{s,sol-liq}}{R} \qquad (22)$$

For ionic solutions:

$$\ln\frac{\prod\left(z_{i,ion}c_{i,ion,liq}\right)^{\nu_i}}{\left(c^{\oplus}\right)^{\sum\nu_i}}=\ln K_{sp}=\frac{-g^{\oplus}_{s,sol-liq}}{RT^{\oplus}}=\frac{-\left(\sum\nu_i g^{\oplus}_{f,i,ion,aq}-g^{\oplus}_{f,s}\right)}{RT^{\oplus}},\quad \frac{d\ln K_{sp}}{d\frac{1}{T}}=\frac{-h^{\oplus}_{s,sol-liq}}{R} \qquad (23)$$

where the solubility-product constant, K_{sp}, has been introduced (it coincides with solubility concentration for non-electrolytes), as well as the ion charge z, and ion stoichiometric coefficient ν (e.g. for $CaCl_2(s)\rightarrow Ca^{2+}(aq)+2Cl^-(aq)$, $z=2$ and $\nu=1$ for $Ca^{2+}(aq)$, whereas $z=1$ and $\nu=2$ for $Cl^-(aq)$).

For instance, for the solution reaction NaCl(s)→Na$^+$(aq)+Cl$^-$(aq), solubility at 25 ºC is $c_{s,liq}$=5.6 mol/L, what corresponds to a solubility-product constant, K_{sp}=5.6·5.6=31, since dissociation is complete at dilute solution, what can be deduced from Thermochemical data of solutes as $K_{sp}=\exp\left[-\left(\sum\nu_i g^{\oplus}_{f,i,ion,aq}-g^{\oplus}_{f,s}\right)/(RT^{\oplus})\right]$=exp(−(−262−131+384)/(8.3·0.298))=exp(3.6)=36, not far from the former value.

The heat of solution of NaCl can also be deduced from Thermochemical data of solutes: $h^{\oplus}_{s,sol-liq}=\left(\sum\nu_i h^{\oplus}_{f,i,ion,aq}-h^{\oplus}_{f,s}\right)$=-240−167−(−411)=4 kJ/mol, positive, implying it cools on adiabatic mixing (i.e. endothermic), what favourably compares with Heat of solution data.

Notice that the equilibrium constant in (23) establishes a relation between the equilibrium concentration of the ions that enter in the dissolving reaction considered, and thus it is independent of the presence of other ions or of the source that produces the ions. For instance, K_{sp}=31 for NaCl(s)→Na$^+$(aq)+Cl$^-$(aq) may correspond to the saturation of pure water with NaCl(s) that reaches a $c_{\mathrm{Na}+}$=5.6 mol/L and $c_{\mathrm{Cl}-}$=5.6 mol/L in the solution at 25 ºC, or it may correspond to the saturation of a hydrochloric solution HCl(aq) with salt, with a lower salt solubility, may be $c_{\mathrm{Na}+}$=4.5 mol/L and $c_{\mathrm{Cl}-}$=6.9 mol/L in the solution at 25 ºC, but still verifying K_{sp}=4.5·6.9=31, or to the saturation of a sodium hydroxide solution NaOH(aq) with salt, with a lower salt solubility that might yield $c_{\mathrm{Na}+}$=6.9 mol/L and $c_{\mathrm{Cl}-}$=4.5 mol/L in the solution at 25 ºC, but still verifying K_{sp}=6.9·4.5=31. As can be seen, the solubility product constant is useful for predicting solubilities of salts not only in pure water, but in solutions which already contain one or the other of the ions in the dissolving substance.

Notice also that there can be strong ionic interaction when two different solutions come in contact, as when a solution of sodium chloride is mixed with a solution of silver nitrate. According to the solubility rules, NaCl and $AgNO_3$ are soluble salts, what makes it possible to prepare a fairly concentrated solution of each salt. Because salts are strong electrolytes, these solutions contain the constituent ions of the salts: Na$^+$(aq), Cl$^-$(aq), Ag$^+$(aq), and NO_3^-, respectively. However, there is a cation-anion combination that produces an insoluble salt: AgCl(s), forming a precipitate, according to the net ionic equation Ag$^+$(aq)+Cl$^-$(aq) → AgCl(s).

Most of the standard thermochemical data originate from electrochemical measurements. For instance, the enthalpy of formation of HCl(aq) is found by building an electrochemical cell to have at equilibrium Cl_2(g)+H_2(g)=2HCl(aq), and the voltage is measured at several temperatures, resulting in $\varepsilon^{\oplus}$=1.36 V and $d\varepsilon^{\oplus}/dT$=−0.00125 V/K, thus $h_f^{\oplus}=zF(Td\varepsilon^{\oplus}/dT-\varepsilon^{\oplus})$=−167 kJ/mol, i.e. the enthalpy of formation of Cl$^-$(aq) shown in Thermochemical data of solutes.

Partition of a solute between two immiscible solvents

Solubility refers to the equilibrium between a pure solute and its solution on a given solvent; for the solubilities of a given solute in two immiscible liquids, the partition coefficient is defined, measuring the concentration of the solute in one of the solutions, divided by the concentration in the other, taken as reference and usually having water as solvent (e.g. the partition coefficient for benzene in the n-octanol/water system is 130, meaning that at 25 ºC, benzene dissolves 130 times more in n-octanol than in water).

Supersaturation. Undercooling and overheating. Hydrates and clathrates

Thermodynamic equilibrium in solutions may take a lot of time if not appropriately stirred (nobody waits for sugar to dissolve in the coffee without stirring), thence it is not difficult to have supersaturated solutions in practice, i.e. solutions with solute-concentrations above the solubility limit. Supersaturation can easily be made by cooling a saturated solution (see Hot pads and cold pads for a good example on undercooling / overheating)

When a supersaturated solutions of a ionic salt starts to crystallise, most of the times a solute-solvent solid compound is formed, named an hydrate in the case of water solutions. Hydrates are chemical compounds (i.e. they follow the law of defined proportions, and the law of multiple proportions when more than one hydrate is formed). The formation energy of hydrates is low because only hydrogen bonds are established, leaving the water molecule nearly intact, and thus, many hydrates are unstable when not in contact with the solvent, and tend to decompose by sublimation of water molecules (efflorescence). Popular hydrated salts are Glauber's salt (sodium sulphate decahydrate, $Na_2SO_4·10H_2O$, used a mild laxative since J. Glauber found it in a Hungarian spring), Epsom salt (magnesium sulphate heptahydrate, $MgSO_4·7H_2O$), calcium chloride hexahydrate ($CaCl_2·6H_2O$), magnesium chloride hexahydrate ($MgCL_2·6H_2O$), and magnesium nitrate hexahydrate ($Mg(NO_3)_2·6H_2O$).

A different kind of solid phase may appear in supersaturated solutions of molecular solutions (and some ionic solutions also): clathrates (from Greek *klaithra*, door bar, or from *kleiein*, to close). Clathrates are spacious crystal lattices that can hold other molecules, i.e. they are solid solutions of the inclusion type (not of substitution). Two main types may be distinguished:

- Stable-lattice clathrates, where a solid-solvent host is stable before inclusion of the guest molecules: e.g. fullerenes, carbon nanotubes, zeolites, etc.
- Stabilised-lattice clathrates, where the liquid solvent host is stabilised in the solid phase by trapped guest molecules: e.g. methane clathrates.

The latter are the most interesting clathrates, and the basic structure is a 3-D solid lattice of H-bonded water molecules enclosing some other small molecule (thence, usually from a gas, but some salts like urea or NaCl too). The lattice stays solid although not all the holes in the lattice are filled with guest molecules, thence, the overall composition is not fixed as in chemical compounds (e.g. as in hydrates); instead, clathrates may be viewed as solid solutions stabilised by a gas-hydrate component (of chemical formula that of the unit cage).

Already in 1823 Faraday found a clathrate, a white crystalline powder of composition $Cl_2·7.3H_2O$. Great interest in clathrates nowadays aims at profiting from natural methane clathrates found in the sea-bed of continental platforms as a huge energy resource, but decades ago the interest was to avoid their formation in natural-gas pipelines to avoid blockage; decomposition of gas hydrates would increase the greenhouse effect, but removal of carbon dioxide from atmosphere by converting it to the hydrate form has also been advocated. Water desalination and gas separation and storage are other possible applications.

Related to clathrates are chelates. A chelate is a chemical compound formed by multiple bonds of a chelating agent (e.g. oxalate ion, $C_2O_4^{2-}$) with a transition-metal ion, resulting in formation of ring structures incorporating the ion (e.g. haemoglobin). The term chelate derives from the Greek word for "claw" and a chelate can be imagined as a claw clasping something to later be released.

Zeolites are the most important class of clathrates from solid hosts. They are micro-porous crystalline tetrahedral structures, built with silicon, aluminium and oxygen atoms, and holding cations, water and/or other molecules within their pores (smaller that 1 nm). Some zeolites (also known as molecular sieves) are now synthesised, are widely used for selective absorption processes, since their porous size can be finely controlled. The cations in zeolites are loose and can be easily exchange by others, what is used for reducing the hardness of water.

Methane clathrate looks like white snow in dispersed state or like greyish ice, and only forms at certain pressure and temperature: e.g. for the system liquid-fresh-water / pure-methane-gas, at 273 K, clathrate forms at pressures >2.6 MPa. Main properties of methane clathrate are: clathrate density ρ=917 kg/m^3, empty water lattice density ρ=796 kg/m^3, specific gas content of 164 m^3 per 1 m^3 of hydrate, speed of sound in the clathrate 3500..3800 m/s, thermal conductivity k=0.5 W/(m·K), thermal capacity c_p=258 J/(mol·K) (at 270 K and hydrate number 6), enthalpy of phase transition (enthalpy of dissociation) from clathrate to gas and ice 18.2 kJ/mol at 273 K, from clathrate to gas and water 54,2 kJ/mol at 273 K.

Density

Ideal mixtures conserve the volume and thermal energy of the components, but real solutions show small volume and temperature changes when mixing. It frequently happens that mixtures with exothermic heats of mixing contract (e.g. 0.5 L water plus 0.5 L methanol yield 0.965 L of solution), while mixtures with endothermic heats of mixing tend to expand.

Notice that solutions stratify a little at equilibrium (see Mixture settling), but a stronger stratification may occur at a metastable equilibrium, as when convection is avoided in some miscible solutions of different concentrations (unassisted diffusion of a substance through a liquid is a rather slow process). Some bizarre multilayer liquid system can be established (taking care to avoid convection), by slowly pouring some glycerol (ρ=1260 kg/m^3) over a syrup (say with ρ=1300 kg/m^3 for 60%wt sugar solution), and adding some liquid detergent (say ρ=1040 kg/m^3), and water (ρ=1000 kg/m^3), and vegetable oil (say ρ=900 kg/m^3), and some alcohol, a good choice being isopropyl alcohol (ρ=785 kg/m^3), because it is non-volatile, and so on.

A linear interpolation in mixture density is sometimes used, $\rho_m=\rho_{dis}+y_s(\rho_s-\rho_{dis})$, besides having no physical bases (for ideal mixtures, the relation is $1/\rho_m=y_{dis}/\rho_{dis}+y_s/\rho_s$, but it gives a poor approximation for non-ideal mixtures, see Fig. 3). Empirical correlations are often used, with a linear form $\rho_m=\rho_{dis}+Ay_s$ for solutions not very concentrated (see Density of solutions data), or higher order polynomials for better fittings. In the linear range, the relative volume-increase by addition of solute is $(V_m-V_{dis})/V_{dis}=(1-A/\rho_{dis})y_s$.

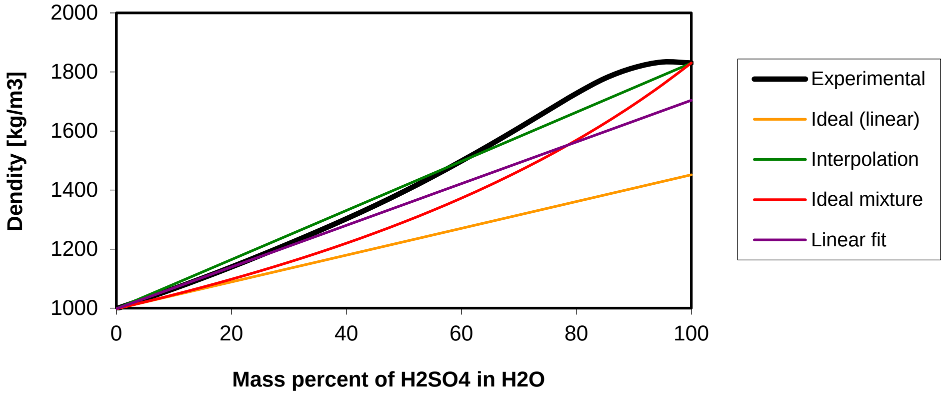

Fig. 3. Comparison of different density models with experimental data for aqueous solutions of sulfuric acid.

A curious application of solution density variations is matching the density of another immiscible liquid, to establish neutral-buoyancy environment (weightless simulation). A simple example is the preparation of a water-alcohol bath with the same density as some oil (vegetal, mineral or synthetic); large oil drops and oil bridges between some supporting solids can be established within the bath, a technique named 'Plateau tank' in honour of the XIX c. Belgian physicist Joseph Antoine Plateau (1801-1883), who performed colourful experiments with bulk liquids (oil within a water-alcohol mixture), and with soap bubbles, around 1870, in spite of being blind since the 1840s by staring at the Sun while performing optical experiments.

Up to here we were referring to density of liquid solutions as a function of concentration, at given temperature and pressure. To analyse the general $\rho=\rho(T,p,x_i)$ relation is another question. For ideal mixtures we say that the molar volume of a mixture was the linear combination of the molar volume of the pure components weighted with their molar fractions, i.e. $v(T,p,x_i)=\Sigma x_i v_i^*(T,p)$, and for pure substances an analytical, numerical or graphical equation of state was used for the whole fluid range (e.g. Redlich-Kwong equation). In the case of mixtures, a similar one-fluid equation (i.e. covering all gas and liquid states) may model $v(T,p,x_i)$ if some ‘mixing rules’ are given to compute the coefficients in terms of those of the pure components. Perhaps the simplest such equation of state for a mixture is the Kay mixing rule model, that proposes to use the corresponding state model with an artificial critical point defined by $p_{cr}=\Sigma x_i p_{cr,i}^*$ and $T_{cr}=\Sigma x_i T_{cr,i}^*$. Another equation-of-state model is based on the Redlich-Kwong equation (see Potentials), defining the two parameters a and b for the mixture as a combination of the two sets of parameters for the pure components (a_1 and b_1) and (a_2 and b_2) in the way::

$$p=\frac{RT}{v-b}-\frac{a}{v(v+b)}\qquad\begin{cases}a=a_1x_1^2+2\sqrt{a_1/a_2}\,x_1x_2+a_2x_2^2\\ b=b_1x_1^2+\left(b_1+b_2\right)x_1x_2+b_2x_2^2\end{cases}\tag{24}$$

More accurate models may introduce the acentric factor and other additional parameters. With additional mixing rules for the thermal capacity of the solution in terms of those of the components, a full thermodynamic model may be built.

Heat of solution

When a solute dissolves in a solvent, the process may be endothermic or exothermic, i.e. the system may warm (or heat be released) or cool (or heat absorbed from the environment). Heat of solution is also known as heat of mixing or heat of absorption, and may be defined globally by $h_r=h_{\text{mixture}}-\sum n_i h_i{}^*$, and measured by calorimetry (measuring the heat exchanged with the surroundings when some amount of solute is added to some amount of solvent, and dividing by the amount of solute added), or differentially as for a generic chemical reactions $h_r{}^{\oplus}\equiv\partial H/\partial n_i|_{T,p}$, which can be computed by differencing the plot of global values as a function of amount of solute.

Most mixtures are mildly exothermic because spontaneous processes must obey $\mathrm{d}G=\mathrm{d}H-T\mathrm{d}S<0$, teaching that exothermic processes ($\mathrm{d}H<0$) are easier to realise than endothermic processes ($\mathrm{d}H>0$), for which a large increase in entropy is required to overcome the enthalpy increase.

As said before, we only consider non-reacting solutions, i.e. we do not take into consideration, for instance, the 'dissolution' of a metal in an acid solution (e.g. $Mg(s)+2HCl(aq)=MgCl_2(aq)+(1/2)H_2$+462 kJ/mol).

The process of dissolving a solid in a liquid is really a two-step process; first, the solid crystal-lattice breaks down in an endothermic process, and second, the individual particles get surrounded by solvent molecules in an exothermic process; the overall process is endothermic or exothermic according to the net balance amongst the two steps. For instance, the endothermic heat of NaCl solution, 3.9 kJ/mol, comes from a lattice energy of 769 kJ/mol and an hydration energy of −765 kJ/mol; the endothermic heat of KCl solution, 17 kJ/mol, comes from a lattice energy of 700 kJ/mol and an hydration energy of −683 kJ/mol. When flour dissolves in water to form dough (1 kg of water per 2 kg of flour), 15 $\mathrm{kJ/kg_{dough}}$ of hydration heat is released.

Dissolving takes a lot of time, with typical relaxation times under normal stirring of some minutes (e.g. the time it takes for a freshly-prepared salt-water solution to become transparent); thus, corrections are often introduced to cope with unavoidable heat transfer to/from the environment.

Some heats of solution at 15 ºC are presented in Heat of solution data, for dilute solutions. Heats of solution decreases somehow with concentration.

Freezing mixtures

Throughout the ages, ice was the traditional cooling agent, and refrigeration technology aimed at producing artificial ice. But ice alone is only useful to cool things but not to freeze them, since most stuff of interest are aqueous solutions with a freezing point below zero. Mixing ice with salt provides the most common freezing mixture, able to cool things down to −21 ºC. Freezing mixtures were first described in Muslim Spain, in the 13th century. It was the Spanish physician Blasius Villafranca who first described, around 1550, that the dissolution of saltpetre (KNO_3) in water lowered its temperature. The first person to freeze water at will seems to have been the Italian physician and professor Latinus Tancredus, in 1607, by putting it in contact with a mix of snow and salt. Endothermic mixing was first explained by Raoult in 1878.

Although there are many other freezing mixtures (see endothermic reactions in Heat of solution data), common salt is the cheapest option (some 1 €/kg against some 30 €/kg for other salts). Sodium chloride forms the eutectic at −21.1 °C and 23.3%wt; magnesium chloride forms the eutectic at −33.6 °C and 21.6%wt, and calcium chloride at −55 °C and 29.8%wt (it can be used to freeze mercury, at −39 °C).

Besides, mixing ice with alcohols (methanol, ethanol, glycols, glycerol) also produce freezing mixtures (crushed ice on a 30%vol ethanol-water spirit, ρ=954 kg/m^3, may lower the temperature down to −19 ºC).

Another application of freezing mixtures may seem paradoxical at first glance: to get rid of ice in roads, since the salt-ice mixture gets cooler and cooler by melting the ice to form a more stable liquid solution.

Cooling with freezing mixtures is a quite vigorous process because of the high thermal conductance of the liquid formed; on the contrary, liquid nitrogen cools by generating a gas that acts as a thermal insulator. For instance, when a commercial cold pouch (see Hot pads and cold pads) containing an aqueous solution of NH_4NO_3(s) with x_s=0.185 (0.227 mol of salt per mol of water), is activated (the salt dissolves), the system temperature, air-insulated, may drop from +15 ºC to −11 ºC. It is important to keep the system well insulated and to stir the freezing mixture. Valuable salts used for freezing mixtures can be recovered by heating the mixture to evaporate the water.

The largest part in the cooling effect of freezing mixtures is due to the melting of ice, but the dissolving of the salt contributes its part as well. Curiously enough, more cooling is achieved by using the hydrated salts (e.g. $CaCl_2·6H_2O$(s)) than the anhydrous components (e.g. $CaCl_2$(s)).

There are other non-machinery freezing means at our disposal. Dry ice is solid carbon dioxide, that at 100 kPa sublimates at -78.5 °C; it is often mixed with liquids like alcohol, acetone, chloroform or ether to make a cooling bath. The temperature, however is not lower than the sublimation temperature of CO_2, and no eutectic is formed. Liquid nitrogen boils at -196 °C and is convenient to use, leaving no clean-up. Both, dry ice and liquid nitrogen are available in cryogenic containers, and can be handled for a short time within simple styrofoam containers.

Exercise 4. Freezing mixture

Colligative properties

Properties that are proportional to the amount of substance and do not depend on the particular substance are called colligative properties. The best example is gas pressure; at low pressures all gases exert a pressure proportional to its amount of substance, $p=nR_uT/V$, independently of the type of gas, and consequently, a mixture of gases will produce a pressure $p=\sum n_iR_uT/V$.

Solutions of non-volatile solutes show several colligative properties: vapour-pressure depression, freezing-point depression, boiling-point increase, and osmotic pressure. Notice that the amount of substance in solution differs from the amount dissolved in the case of electrolytic solutions.

It was Raoult who, from 1878 onwards, first tabulated the freezing points of many solutions, and other parameters (he made many publications just on this topic).

Vapour-pressure depression

It is the decrease of the vapour pressure of a solvent by a non-volatile solute (the effect is called tonoscopy). In the ideal mixture limit, Raoult's law,

$$p_v = p_v^*(1 - x_s) \tag{25}$$

where p_v^* is the vapour pressure for the pure solvent; e.g. distilled water has a vapour pressure of 3.17 kPa at 25 ºC (as can be measured by letting boiling water in a flask to cool down after closing the flask); thence seawater at 25 ºC will have a vapour pressure of 3.11 kPa, because seawater has approximately 35 g NaCl per kilogramme of solution, and most of it is dissociated (one mole NaCl yields two moles of solutes). That is why fresh water evaporate faster than seawater (if three equal glasses with the same amount of tap water are exposed to ambient air, and one spoon of sugar is added to one, and one spoon of salt to other, the fresh water evaporate faster than the sweet water, and that faster than the salt water.

Freezing-point depression

It is the decrease of the freezing point of a solvent by a volatile or non-volatile solute (e.g. CO_2(g) or NaCl(s) in water). This effect is called cryoscopy. In the ideal mixture limit:

$$T_f = T_f^* - \frac{RT_f^{*2}}{h_{SL}} x_s = T_f^* - \frac{RT_f^{*2}}{h_{SL}} \frac{m_s}{\rho^* / M^*} = T_f^* - K_f m_s \tag{26}$$

where m_s is the solute molality and K_f is known as the cryoscopic constant; e.g. distilled water has the freezing point at 0 ºC (the influence of pressure is negligible here) and K_f =1.86 K/(mol/L), whereas seawater with y_s=0.035 (or around 1.2 molal) has its freezing point at –1.9 ºC. See Cryoscopic and ebullioscopic data for freezing-point depression data.

Boiling-point increase

It is the increase of the boiling point of a solvent by a non-volatile solute (the effect is called ebullioscopy). In the ideal mixture limit:

$$T_b = T_b^* + \frac{RT_b^{*2}}{h_{LV}} x_s = T_b^* + \frac{RT_b^{*2}}{h_{LV}} \frac{m_s}{\rho^* / M^*} = T_b^* + K_b m_s \tag{27}$$

where m_s is the solute molality and K_b is known as the ebulloscopic constant; e.g. distilled water has the boiling point at 99.7 ºC at 100 kPa (the influence of pressure cannot be neglected here) and K_b=0.52 K/(mol/L), whereas seawater has its freezing point at 100.3 ºC. Trouton's rule, $h_{LV}/(RT_b)\approx 10$, indicates that K_b is proportional to solvent boiling-point temperature (see Cryoscopic and ebullioscopic data).

Osmotic pressure

It is the pressure-difference due to a difference in concentration of a solute between two solutions of the same solvent in contact through a semi-permeable membrane (the effect is named osmosis). In the ideal mixture limit:

$$p = p^* + n_s RT / V \tag{28}$$

e.g. if distilled water and seawater are put in contact through a semi-permeable membrane that only lets water molecules to pass and not big ions as Na^+ or Cl^-, an overpressure of 2.7 MPa must be applied to the seawater-side to maintain equilibrium and prevent water molecules to pass from the pure water side to dilute the strong solution.

Most of these colligative properties can be used for chemical analysis, i.e. to characterise a species in a mixture, by finding the molar mass of the solute from the change in freezing or boiling point of the mixture (better from freezing point depression, because it is larger), or from osmotic pressure measurements, etc.

It should be stressed that, although in many instances the addition of a solute to a solvent lowers its freezing point and increases its boiling point, this is mostly for non-volatile solutes; other solutes may have the opposite influence (e.g. adding a small amount of water to methanol increases its vapour pressure, whereas adding water to propanol lowers it. Related to that is the fact that some solvent-solution couples may behave asymmetrically and others symmetrically in certain cases; e.g. a small amount of methanol lowers the boiling point of water but a small amount of water increases boiling point of methanol, whereas a small amount of ethanol lowers the boiling point of water and a small amount of water also lowers the boiling point of ethanol.

Properties of particular solutions

Thermochemical data of solutes

Solubility data for aqueous solutions

Density data for solutions

Heat of solution data

Cryoscopic and ebullioscopic data

Back to Index