# Multicomponent Phase Equilibria

(Intensive) equilibrium criteria call for equal chemical potential (or fugacity) of a given compound in all coexisting phases, e.g. for a two-phase system $\mu_i^1 = \mu_i^2 \Longleftrightarrow f_i^1 = f_i^2$.

## *l-g* Equilibrium: Raoult's Law

In an equilibrium liquid-gas system with the assumption of ideal behavior of gaseous components the equilibrium condition is

$$p y_i = \gamma_i p_i^{\otimes} x_i$$

where $y_i$ is molar fraction in gas phase and $x_i$ molar fraction of the same component in the liquid phase. This equation is often called **Raoult's law**. Calculating the equilibrium composition requires the knowledge of vapor pressure and activity coefficients of all components in the liquid phase. Activity coefficients can be estimated e.g. from Redlich-Kister equation or Wilson equation, most commonly the estimates are based on structure-activity relationships such as the UNIFAC. On the other hand, experimental evaluation of activity coefficients is often based on phase equilibrium measurements. The equilibrium in binary systems can be represented in a graphical form, either in isobaric (temperature-composition), isothermal (pressure-composition) or isobaric-isothermal (vapor-liquid composition) diagrams.

## *l-l* Equilibrium: Extraction, Nernst Distribution Law, Partition Coefficient Water - Octanol

During **extraction** the solute is partially transported from solvent 1 to solvent 2. The two solvents must be mutually immiscible (one solvent can actually be solid). Equilibrium is described by partition coefficient (= equilibrium constant for a transport of solute between solvents 1 and 2)

$$K_c = \frac{a_2}{a_1} \approx \frac{c_2}{c_1}$$

where $a_2$, $a_1$ a $c_2$, $c_1$ are activities and concentrations, respectively, in solvents 2 and 1. This relation is known as **Nernst distribution law**. If $n_0$ is the initial amount of extracted solute in volume $V$ of solvent 1 and $n_p$ is the amount of solute, transported by extraction to solute 2 with volume $L$, we fid

$$n_p = n_0 \frac{K_c L}{V + K_c L}$$

$k$-times repeated extraction with always the same volume $L$ of pure solvent 2 leads to remaining amount $n_z$ in solvent 1

$$n_z = n_0 - n_p = n_0 \left( \frac{V}{V + K_c L} \right)^k$$

One specific case of extraction is the transport of (mainly organic) solutes between water and octanol. Partition coefficient $K_{ow}$ for a given compound is often applied as a model for its distribution among environmental compartments, namely for estimates of bioconcentration factor or for calculating the uptake of pharmaceuticals (octanol serves as a model for lipids and other body tissues).

*Data Sources*: Mackay D., Shiu W.Y., Ma K.C.: Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Lewis Publishers Inc., Chelsea, Michigan, 1992.

*Estimation Methods*: Octanol – water partition coefficient can be estimated e.g. by structure-activity relationships such as the method of Meylan and Howard: Meylan W.M., Howard P.H.: J. Pharm. Sci., 84, 83 (1995).

## Equilibrium in Aqueous Solutions: Solubility of Gases, Liquids and Solids, Salting-Out Effect

### Gases – Henry's Law

Chemical potentials of a solute in (aqueous) solution and in the co-existing vapor phase must be equal, $\mu_i^{aq} = \mu_i^g$

$$\mu_i^g = \mu_i^{ig} + RT \ln(f_i / p^{\circ}) \qquad\qquad \mu_i^{aq} = \mu_i^{\circ} + RT \ln(x_i \gamma_i^{[x]})$$

where $\mu_i^{\circ}$ and $\mu_i^{ig}$ are standard chemical potentials in the aqueous solution and in the ideal gas, $f_i$ is the fugacity of a solute and $x_i$ is its molar fraction in the solution. Combining the above equations we get

$$\mu_i^{\circ} - \mu_i^{ig} = \Delta G_{hyd} = RT\ln\left(f_i/(p^{\circ}x_i\gamma_i^{[x]})\right) = RT\ln\left(k_H/p^{\circ}\right)$$

Transfer from ideal gas standard state to aqueous solution (at the standard state of unit concentration, extrapolated to infinite dilution) is called hydration. The difference of respective chemical potentials is therefore hydration Gibbs energy, $\Delta G_{hyd}$. Henry's law constant $k_H$ is defined as

$$k_H = f_i/x_i\gamma_i^{[x]} \qquad \text{or, more appropriately} \qquad k_H = \lim_{x_i \to 0}\left(f_i/x_i\right)$$

Solubility data are available either explicitly ($mol/m^3$, $g/m^3$ etc.) or can be deduced from Henry's law constant or from the above equations with data on $\mu_i^{\circ}$ and $\mu_i^{ig}$. Fugacity of solute in the vapor phase, assuming its ideal behavior, is equal to partial pressure, $f_i = py_i$. Gas solubility is then

$$x_i = y_i p/(k_H\gamma_i^{[x]})$$

**Liquids and Solids**

Fugacity of a solute is $f_i = x_i\gamma_i f_i^{\circ}$ and equal to its fugacity in the pure liquid or solid state $f_i = f_i^{\circ}$. It follows that

$$x_i = 1/\gamma_i \qquad\qquad k_H = f_i^{\circ}\gamma_i/\gamma_i^{[x]}$$

Fugacity of pure liquid or solid is its vapor pressure. For dilute solutions, the (symmetric) activity coefficient is close to its value at infinite dilution, $\gamma_i \cong \gamma_i^{\circ}$, asymmetric coefficient $\gamma_i^{[x]} \cong 1$ and the equations are simplified to

$$x_i = 1/\gamma_i^{\circ} = p_i^{\otimes}/k_H \qquad\qquad k_H = p_i^{\otimes}\gamma_i^{\circ} = p_i^{\otimes}/x_i$$

If the solid is dissociating electrolyte, dissolution corresponds to reaction $AB(s) = A^{+}(aq) + B^{-}(aq)$ and solubility calculation is the same as for any chemical equilibrium (see example 2 in the lecture on chemical equilibrium). For calculation we need activity coefficients of ions in the solution and standard chemical potentials of ions and the pure solid, or the equilibrium constant for dissolution (**solubility product**).

Presence of an electrolyte in the solution changes solubility of other species. Most often, the solubility in electrolyte is lower than in pure solvent (**salting-out effect**). The change is reflected in the value of activity coefficient. If the solute is also an electrolyte, its activity coefficient can be estimated from Debye-Hückel equation that explicitly depends on the ionic strength of the solution. For nonelectrolyte solutes the effect can be described e.g. by an (empirical) Setchenow equation

$$k_H = k_H^{\circ} + k_S I$$

where $I$ is the ionic strength of the solution and $k_S$ Setchenow (salting-out) coefficient.

_Data Sources_: Henry's law constants – Webbook, solubility of many inorganic compounds is available in common physical or chemical handbooks, standard chemical potentials of minerals and aqueous ions can be obtained e.g. from the database of SUPCRT92 software (web: zonvark.wustl.edu/geopig/ , available at the Department of Chemistry).

_Estimation Methods_: Group additivity method for standard chemical potentials and Henry's law constants or organic solutes: Šedlbauer J., Bergin G., Majer V.: AIChE J., 48, 2936, 2002.

_Conversion of standard states for chemical potential_: Limiting conversion relations between $m_i$ and $c_i$ are

$$\lim_{x_i \to 0} m_i = x_i/M_1 \qquad\qquad \lim_{x_i \to 0} c_i = x_i\rho_1/M_1$$

where $M_1$ is molar mass of solvent in $kg.mol^{-1}$ and $\rho_1$ is the density of solvent in $kg.dm^{-3}$. Using these relations, it holds

$$\mu_i^{\circ[x]} = \mu_i^{\circ[m]} - RT\ln(M_1) = \mu_i^{\circ[c]} - RT\ln(M_1/\rho_1)$$

**Homework 7:** Calculate the concentration of dissolved atmospheric (oxygen; nitrogen; argon; carbon dioxide; sulfur dioxide – use the average concentration measured at a meteorological station in Liberec or nearby). Provide the result in grams of solute per 1 liter of water at ambient conditions.