

Electronic Supplement: Appendices

A1 Single solute molalities and water uptake

In correspondence to Figures 2a and b, Figures A1a and b show the single solute molalities and the associated water uptake of all compounds listed in Table 1.

A2 Equilibrium Thermodynamics

We follow the “classical” thermodynamics to derive the relevant equations for chemical equilibrium, in accord with basic textbooks (e.g. Denbigh, 1981). “Classical”, since water is generally omitted in equilibrium equations unless explicitly involved in the reaction, based on the assumption that water is neither consumed nor produced. However, when hydration is involved, water is consumed and released, which actually causes inconsistencies in the “classical” treatment.

A2.1 Gibb’s free energy

The general condition for thermodynamical and chemical equilibrium is that the total free energy of the system – usually referred to as Gibb’s free energy (G) – is at a minimum, which implies that $dG = 0$ (see e.g. Denbigh, 1981).

The Gibb’s free energy expresses the sum of total free energies of the system, $G \equiv U + PV - TS$, by which the first term on the rhs denotes internal energy (U), and is always positive. The second term accounts for the energy associated with either changing a volume (V) at constant pressure (P), or by changing the pressure at constant volume; and can be either negative (e.g. by expansion) or positive (e.g. by compression). The third term accounts for the energy that is associated with the degree of order of the system at given temperature (T) and entropy (S), and is always positive.

Any differential change in G yields

$$dG = dU + PdV + VdP - TdS - SdT = 0, \quad (\text{A1})$$

by which at constant temperature ($dT = 0$) the entropy term (SdT) disappears. At constant pressure ($dP = 0$), Eq. (A1) reduces to

$$dG = dU + PdV - TdS = 0. \quad (\text{A2})$$

With the definition of the internal energy, $U = TS - PV + \mu n$, which is known as the Euler equation, any differential change in U leads to (at constant T and P)

$$dU_{|T,P} = TdS - PdV + \mu n, \quad (\text{A3})$$

by which $SdT - VdP + n d\mu = 0$ is known as the Gibbs-Duhem equation. It shows that three intensive variables are not independent (T, P , and μ are intensive, the others extensive) – if one is known, the value of the third can be determined from the Gibbs-Duhem equation.

Upon substitution of Eq. (A3) in Eq. (A2), i.e. eliminating dU with the Gibbs-Duhem relation, we can express dG in terms of a concentration change, which is zero when the j -th chemical reaction that forms compound j reaches equilibrium, i.e.

$$dG_{|T,P}^j = \sum_{i=1}^k \mu_{ij} dn_{ij} = 0; \quad (\text{A4})$$

n_{ij} denotes the amount of the i -th of k components and μ_{ij} its chemical potential.

A2.2 Equilibrium constant

For the j -th chemical reaction, the amount of each component is $n_{ij} = n_{ij}^o + \nu_{ij}\varepsilon_j$, where n_{ij}^o is the initial amount of each component; ν_{ij} is their stoichiometric coefficient and ε_j their reaction coordinate.

Taking the derivative of n_{ij} , i.e. $dn_{ij} = \nu_{ij} d\varepsilon_j$ with $d\varepsilon_j = 1$, when substituted into Eq. (A4) gives

$$\sum_{i=1}^k \mu_{ij} dn_{ij} = 0. \quad (\text{A5})$$

The chemical potentials μ_{ij} are usually expressed in terms of their activities a_{ij} , i.e. $\mu_{ij} = \mu_{ij}^o + RT \cdot \ln a_{ij}$. μ_{ij}^o denotes the chemical potential at a standard state and equals the partial molar Gibbs free energy g_{ij}^o with units in kilo Joule [kJ/mol]; R [J/molK] denotes the universal gas constant, T [K] the temperature. Upon substitution into equation (A5), i.e.

$$\sum_{i=1}^k \nu_{ij} g_{ij}^o + RT \cdot \sum_{i=1}^k \nu_{ij} \ln a_{ij} = 0. \quad (\text{A6})$$

which yields upon rearranging and exponentiation, with expressing the sum of the logarithm as their product, the equilibrium constant (K_j) for the j -th chemical reaction at given temperature (T), i.e.

$$K_j = \exp\left(-\sum_{i=1}^k \nu_{ij} g_{ij}^o / RT\right) = \prod_{i=1}^k a_{ij}^{\nu_{ij}}. \quad (\text{A7})$$

The temperature dependency of the equilibrium constant is calculated from the van't Hoff equation (now dropping the index j), i.e.

$$d \ln K / dT = \Delta H_f(T) / (RT^2), \quad (\text{A8})$$

where $\Delta H_f(T)$ is the standard molar enthalpy change of formation of the j -th compound at temperature T . For a small temperature change ΔH_f can be approximated by

$$\Delta H_f(T) = \Delta H_f^o(T^o) + \Delta C_p^o(T - T^o). \quad (\text{A9})$$

$\Delta H_f^o(T^o)$ denotes the standard molar enthalpy change of the reaction at a reference temperature T^o , (usually the standard-state temperature 298.15 K), and $\Delta C_p^o(T - T^o)$ the change of the standard molar heat capacity at constant pressure compared to T^o ; it is implicitly assumed here that ΔH_f^o and ΔC_p^o are constant over the temperature range $T - T^o$.

Substituting Eq. (A9) into Eq. (A8) and integrating over $T - T^o$, the temperature dependency of the equilibrium constant is obtained, i.e.

$$K(T) = K^o(T^o) \cdot \exp \left[-\Delta H_f^o / (RT^o) \cdot (T^o/T - 1) - \Delta C_p^o / R (1 + \ln(T^o/T) - T^o/T) \right]. \quad (\text{A10})$$

The data on ΔG^o , ΔH_f^o , and ΔC_p^o (needed to calculate equilibrium constants and their temperature dependency) can be obtained for instance from the CRC Handbook of Chemistry and Physics (2006).

Finally, the activities (used in Eq. A7) of single-salt solutions consist of \pm -ion pairs, whereas the i -th components \pm -ion pair activity is usually expressed as (Robinson and Stokes, 1965)

$$a_{i\pm}^{v_{\pm}} = (\gamma_{\pm} m_{\pm})^{v_{\pm}} = a_+^{v_+} a_-^{v_-} = (\gamma_+ m_+)^{v_+} (\gamma_- m_-)^{v_-} = \gamma_{\pm}^{v_{\pm}} m_+^{v_+} m_-^{v_-}. \quad (\text{A11})$$

v_+ and v_- denote the number of moles of cations and anions per 1 mol of solute (\pm -ion pair) dissociating completely into $v_{\pm} = v_+ + v_-$ ions. m_{\pm} , m_+ , m_- denote the corresponding molalities, i.e. the concentration of the ions in the solution, by which the molality is defined as mole solute per kg solvent (water). $\gamma_{\pm}, \gamma_+, \gamma_-$ are the dimensionless mean binary activity coefficient of the \pm -ion pair, and the activity coefficients of the cations and anions, respectively. The activity coefficients are introduced to correct the solution molalities for non-ideality at higher solute concentrations due to ion-ion interactions.

Eq. (A7) becomes in terms of activity coefficients and molalities

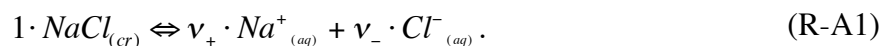
$$K_j = \prod_{i=1}^k (\gamma_{ij\pm} m_{ij\pm})^{v_{ij\pm}}, \quad (\text{A12})$$

where the subscript i denotes i -th component (\pm -ion pair) of the j -th compound (reaction).

Since K_j is a characteristic constant for the j -th chemical equilibrium reaction and usually determined with the aid of Eq. (A7) from experimentally gained thermodynamic data, Eq. (A12) enables to relate and calculate various solute properties that are difficult to measure, as for instance solute activities (a_{ij}), molalities (m_{ij}) and activity coefficients (γ_{ij}) of \pm -ion pairs, or of the individual cations and anions. However, the summation over i is usually only made over the k -components that form the j -th compound, by which water is usually by definition omitted, as long it is neither consumed nor produced – even when being essential for the equilibrium reaction to take place.

A2.3 Example

For instance, for the example illustrated in Figure 1b), the stoichiometrical (i.e. on a molar basis) reaction of the dissociation of crystalline (cr) sodium chloride ($NaCl$) \pm -ion pair into the aqueous (aq) sodium (Na^+) cation and chloride (Cl^-) anion is



The corresponding equilibrium constant for this j -th reaction (R1) with its i -th components gives

$$K_{NaCl_{(cr)}} = [Na^+_{(aq)}]^{\nu_+} + [Cl^-_{(aq)}]^{\nu_-} \cdot \gamma_+^{\nu_+} \gamma_-^{\nu_-}, \quad (K-A1)$$

by which $K_{NaCl_{(cr)}}(T^o) = 37.661 [mol^2/kg^2]$ with the constants $a = -\Delta H_f^o / (RT^o) = -1.56$ and $b = \Delta C_p^o / R = 16.9$ that are needed to calculate the temperature dependency according to Eq. (A10); $RT^o = 8.314 [J/mol/K] \cdot 298.15 [K] = 2.479 [KJ/mol]$.

A2.4 Solubility

Although the above also applies to the calculation of the solubility constants, there are however some peculiarities about solubility equilibria that help apply important simplifications, despite the fact that solubility calculations can become quite complex, especially when involving complex-ion equilibria that allow to dissolve an insoluble salt.

First, at equilibrium the solution is saturated, i.e. it contains the maximum concentration of ions that can exist in equilibrium with its solid (crystalline) phase. In this case the ion concentrations of $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ are sufficiently high so that the rate at which precipitation occurs exactly balances the rate at which $NaCl_{(cr)}$ dissolves. Thus, there is no change in the concentration of these ions with time when the reaction is at equilibrium. The amount of solute that must be added to a given volume

of solvent to form a saturated solution is called the solubility of the solute. In other words, if the system is at equilibrium the ion product, which is the product of the concentrations of the ions, equals the solubility product for the solute. If the ion product is larger or smaller than the solubility product for the solute, the system not at equilibrium, but the system can rapidly adjust according to Le Chatelier's principle, so that equilibrium is restored after the excess ions precipitate from solution as a solid ($NaCl_{(cr)}$), or a solid dissolves until any deficit in the ion product is compensated. Thus, the solubility constant expression for reaction (AR1) can be calculated from (AK1) when divided by the concentration of the solid, by which the concentration of a solid ($NaCl_{(cr)}$) is calculated from its density and its molar mass. For instance, for solid $NaCl_{(cr)}$, i.e.

$$\frac{\rho_{NaCl_{(cr)}}}{1 \text{ cm}^3} = \frac{2.17 \text{ g } NaCl_{(cr)}}{1 \text{ cm}^3} \times \frac{1 \text{ cm}^3}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol } NaCl_{(cr)}}{58.44 \text{ g } NaCl_{(cr)}} = 37.13 \text{ mol } NaCl_{(cr)} / \text{L}. \quad (\text{A13})$$

Since the concentration of the solid is constant, which has no effect on the equilibrium, it is built into the solubility constant for the equilibrium reaction. According to (K-A1) we have

$$K_{sp, NaCl} = K_{NaCl_{(cr)}} \cdot a_{NaCl_{(cr)}} = a_{Na^+}^{v_+} \cdot a_{Cl^-}^{v_-}, \quad (\text{K-A2})$$

by which (K-A2) is a constant, which is proportional to the solubility of the salt and hence called the solubility product equilibrium constant ($K_{sp, NaCl}$) for reaction (R-A1). Furthermore, the solubility product constant requires that v_+ cations ($Na^+_{(aq)}$) are released for v_- anions ($Cl^-_{(aq)}$), because there is no other source of either ion in this solution, so that the concentrations of the ions at equilibrium are the same, i.e.

$$a_s^{v_s} = a_+^{v_+} = a_-^{v_-}. \quad (\text{A14})$$

In general, it is assumed that salt solutes dissociate into their ions when they dissolve in water. Ionic compounds dissolve in water if the energy released when the ions interact with water molecules compensates for both a) the energy needed to break the ionic bonds in the solid and b) the energy required to separate the water molecules so that the ions can be inserted into solution.

A2.5 Nernst equation

For charged species, the electrical force must be considered, by which the potential for an electrochemical reaction is described by (Nernst, 1889) i.e.

$$E = E^o - R T / (z F) \ln(Q_c). \quad (\text{A15})$$

In the Nernst equation (A15), $E [V]$ is the electrochemical cell potential at some moment in time, $E_o [V]$ the cell potential when the reaction is at standard-state conditions, $R [J/mol/K]$ the ideal gas constant in joules per mole and Kelvin, $T [K]$ the temperature in Kelvin, $z [1/mol]$ the number of moles of electrons transferred in the balanced equation for the reaction, $F = 96484 [C mol^{-1}]$ the Faraday-constant that expresses the charge on a mole of electrons (calculated from Avogadro's number and the charge on a single electron ($F = 6.022045 \times 10^{23} [mol^{-1}] \cdot 1.6021892 \times 10^{-19} [As/e^-]$)), and Q_c the reaction quotient. The magnitude of the cell potential is a measure of the driving force behind a reaction. The larger the value of the cell potential, the further the reaction is from equilibrium, while at equilibrium ($\Delta G = 0$) the overall cell potential $E [V] = 0$. Since then the reaction quotient equals the equilibrium constant ($Q_c = K_c$), the Nernst equation is related to the partial Gibbs free energy by, i.e.

$$g^o = \pm z F E^o = RT \ln(K_c), \quad (A16)$$

and can hence be used to measure the equilibrium constant for a reaction.

The condition that the overall cell potential is zero at equilibrium ($E = 0$) implies electroneutrality, so that the ability of the solution to conduct an electric current by the ions of the solute that result from dissociation must be compensated for a binary solution (one solute and solvent) by an ion flow that results from the dissociation of the solvent (water), by which 2 moles of water will be consumed, i.e. $2 H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$. Since measurements suggest that the ability of pure water to conduct an electrical current at $25^\circ C$ contains $1.0 \times 10^{-7} [mol/L]$ moles per liter of each of these ions, i.e. $[H_3O^+_{(aq)}] = [OH^-_{(aq)}] = 1.0 \times 10^{-7} [mol/L]$, by which their product remains constant at equilibrium, which yields upon the multiplication with the molar concentration of water, the water dissociation equilibrium constant, $K_w = 1.0 \times 10^{-14}$; one kilogram of pure water always contains $1000 [g] / M_{H_2O} [g/mol] = 1000/18.015 = 55.5093 [mol]$.

Although K_w is defined in terms of the dissociation of water, this equilibrium constant expression is equally valid for solutions of acids and bases dissolved in water. Regardless of the source of the $H_3O^+_{(aq)}$ and $OH^-_{(aq)}$ ions in water, the product of the concentrations of these ions at equilibrium at $25^\circ C$ is always $1.0 \times 10^{-14} [mol^2 L^{-2}]$. Thus adding an acid or base to water therefore has an effect on the concentration of both the $H_3O^+_{(aq)}$ and $OH^-_{(aq)}$ ions; they can be hence related in terms of the definition of a negative of the logarithm by $pH + pOH = 14$, with $pH = -\log[H_3O^+_{(aq)}]$ and $pOH = -\log[OH^-_{(aq)}]$.

Similarly, the discussion can be extended to acid/base-dissociation equilibria, including cation-acids and anion-bases, which yield accordingly pK_a and pK_b values that indicate the strength of the acid or base, respectively. However, for chemical reactions involving hydration the assumption that water can be omitted in equilibrium reactions does not really hold, since water is actually consumed by hydration. Neglecting water in equilibrium reactions therefore introduces a conceptual problem and unnecessarily complicates the equations. In the present work we therefore reformulate chemical equilibrium to include water and exploit the implications for atmospheric aerosol modeling.