EQUILIBRIUM EQUATIONS

We give some hints on how to set up mathematical equations for chemical equilibrium problems.

0.1. **Chemical equilibrium.** Consider an elementary reaction of the form

$$\mathrm{AB} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} \mathrm{A} + \mathrm{B} \tag{1}$$

Chemical equilibrium means that the rates of formation of the substances are zero:

$$0 = \frac{d}{dt}[\mathrm{AB}] = -\frac{d}{dt}[\mathrm{A}] = -\frac{d}{dt}[\mathrm{B}] = -k_{11}[\mathrm{AB}] + k_{12}[\mathrm{A}][\mathrm{B}],$$

so that

$$\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{AB}]} = K, \tag{2}$$

where the equilibrium constant is $K = \frac{k_{11}}{k_{12}}$, measured in the unit M = molar = mol/L. In order to use Newton's method we write the equation in the form

$$Kx_1 - x_2x_3 = 0,$$

or

$$x_1 - x_2x_3/K = 0,$$

where $x_1 = [\mathrm{AB}]$, $x_2 = [\mathrm{A}]$, $x_3 = [\mathrm{B}]$.

0.2. **Solubility product.**

$$\mathrm{AB(s)} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} \mathrm{A(aq)} + \mathrm{B(aq)} \tag{3}$$

Here we cannot speak of the concentration of the solid AB and instead of (2) we have

$$[\mathrm{A}][\mathrm{B}] = K_{\mathrm{sp}},$$

where K_{sp} is the solubility product with unit M^2. This leads to the equation

$$K_{\mathrm{sp}} - x_2x_3 = 0,$$

or

$$1 - x_2x_3/K_{\mathrm{sp}} = 0.$$

0.3. **Mass balance.** We need more equations. One possibility is to note that in (1) or (3) we must have

$$V\big([\mathrm{AB}] + [\mathrm{A}]\big) = \mathrm{A}_{\mathrm{tot}}$$

where V is the volume and $\mathrm{A}_{\mathrm{tot}}$ is the total amount of A (mol) which may be known.

0.4. **Charge balance.** Further equations may be obtained by counting the charge of the ions. For example, if AB is neutral and A positive and B negative, then

$$[\mathrm{A}] - [\mathrm{B}] = 0,$$

means that the solution is electrically neutral. `/stig`