# 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

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

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

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

so that

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

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

0.2. **Solubility product.**

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

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

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

where $K_{\mathrm{sp}}$ is the solubility product with unit $\mathrm{M}^2$. 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

$$[\mathrm{B}] = [\mathrm{C}],$$

which leads to the equation

$$x_2 - x_3 = 0.$$

/stig

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