

26.11: Thermodynamic Equilibrium Constants Are Expressed in Terms of Activities

The above is a general principle that can be extended to other concentration units and to liquid solutions, ideal or not. In non-ideal systems we could replace

$$\mu_i = \mu_i^\ominus + RT \ln P_i/P_i^\ominus$$

by:

$$\mu_i = \mu_i^\ominus + RT \ln a_i$$

and follow the same procedure as above. In stead of an expression for K involving pressures or concentrations it now read in **activities**:

$$K = [a_{\text{eq},Y}^{\nu_Y} a_{\text{eq},Z}^{\nu_Z} / a_{\text{eq},A}^{\nu_A} a_{\text{eq},B}^{\nu_B}]$$

For each species we could write the activity as:

$$a_i = \gamma_i c_i / c_i^\ominus$$

Here c_i^\ominus is unity in whatever concentration measure we wish to choose. Again its function is to cancel the dimension of c_i .

With this split in three factors we can write K as three factors as well:

$$K = K_\gamma K_c / K_{c^\ominus}$$

$$K_\gamma = [\gamma_{\text{eq},Y}^{\nu_Y} \gamma_{\text{eq},Z}^{\nu_Z} / \gamma_{\text{eq},A}^{\nu_A} \gamma_{\text{eq},B}^{\nu_B}]$$

$$K_c = [c_{\text{eq},Y}^{\nu_Y} c_{\text{eq},Z}^{\nu_Z} / c_{\text{eq},A}^{\nu_A} c_{\text{eq},B}^{\nu_B}]$$

$$K_{c^\ominus} = [c_{c^\ominus}^{\nu_Y} c_{c^\ominus}^{\nu_Z} / c_{c^\ominus}^{\nu_A} c_{c^\ominus}^{\nu_B}]$$

The last factor is unity, it cancels the dimensions of K_c and is often *omitted*. The factor K_γ is unity *if the solution is ideal*. Obviously, for ionic solutions that is seldom the case.

activities of pure condensed phases

Sometimes one of the reactants or products is a pure solid (precipitate) or liquid (more solvent e.g.). What activity should we assign in such a case?

We start by choosing a suitable standard state, say the pure compound at 1 bar and temperature of interest, we then have:

$$\mu = \mu^\ominus$$

but also:

$$\mu = \mu^\ominus + RT \ln a$$

So $a=1$ at standard conditions

Any change can be written as

$$d\mu = RT d \ln a$$

We can study the pressure dependence by considering:

$$\partial \mu / \partial P |_{T} = V_{\text{partial molar}} (V_{\text{bar}})$$

For a solid or liquid V_{bar} is a relatively small and constant value. Thus we can write:

$$d\mu = V_{\text{bar}} dP$$

$$RTd\ln a = V_{\text{bar}}dP$$

$$d\ln a = V_{\text{bar}}dP/RT$$

Upon integration to a different pressure P' we find

$$\ln a' = (P'-1) V_{\text{bar}}/RT$$

S&McQ

1083

Example 26-12 shows that for graphite the activity is only 1.01 at 100 bars, so the activity is *not* very pressure dependent. Mostly if pure condensed compounds are involved in reactions the activity can be taken as **unity**.

This is also in line with what we said previously about the solvent following Raoult's law. In the limit of the solvent going to pure solvent we have that its P goes to P^* . As the activity is defined as P/P^* this converges to unity. If a reaction produces more solvent molecules we can usually consider their activity equal to one in very good approximation for dilute solutions, even if they are already non-ideal.

The fact that $a=1$ for pure condensed phases has an important consequence for reactions (in general: processes) that only involve such phases. If all activities are unity, $Q=1$ and $\ln Q=0$ which means that $\Delta_r G = \Delta_r G^\ominus + 0$. Thus $\Delta_r G$ can only be zero -i.e. an equilibrium achieved- **if** $\Delta_r G^\ominus$ happens to be zero, which is generally not the case. In fact there can only be an equilibrium at one specific temperature:

$$\Delta_r G^\ominus = 0$$

$$\Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$T_{\text{equilibrium}} = \Delta_r H^\ominus / \Delta_r S^\ominus$$

If the process is the transformation from a solid to a liquid this is the well-known *melting point*. At temperature other than 0°C only one phase can exist: either ice or water. If the other is present, that is an unstable condition and it will transform *entirely* to the stable form. In other words the process will go to completion, *not* equilibrium. Only *at* 0°C can the two coexist in equilibrium. This holds for all melting points but it also holds for e.g. a solid-solid chemical reactions only producing, say, another solid.

Another way of expressing the above is to say that in order to have equilibrium at a *series* of temperatures, one needs at least one species involved for which activity depends on composition, e.g. a dilute solute or a gas.

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