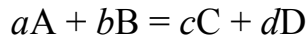


Equilibrium Constant

Consider the general reaction:



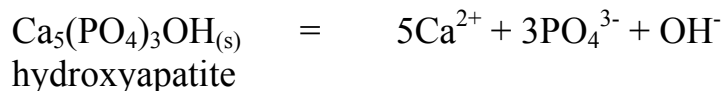
$$\Delta G_R = G_{\text{products}} - G_{\text{reactants}}$$

$$G_{\text{products}} = c(\Delta G_{f,c}) + d(\Delta G_{f,d}) \quad \text{right hand side of the reaction}$$

$$G_{\text{reactants}} = a(\Delta G_{f,a}) + b(\Delta G_{f,b}) \quad \text{left hand side of the reaction}$$

ΔG , ΔH , ΔS are all calculated in the same way.

Let's use the dissolution of hydroxyapatite:



First, for every chemical reaction you need to check that it is balanced.

We calculate ΔG_R , ΔH_R , and ΔS_R by taking the sum of the products (appearing on the right hand side of the equation) minus that of the reactants (species on the left side of the equation). The ΔG , ΔH , and ΔS for each species is the formation multiplied by its coefficient in the chemical reaction.

Source 3	ΔG°_f	ΔH°_f	S°
in Eby	kJ/mol	kJ/mol	kJ/mol K
Hydroxyapatite	-6338.4	-6721.6	390.4×10^{-3}
Ca^{2+}	-553.5	-542.8	-53.1×10^{-3}
PO_4^{3-}	-1019.0	-1277.0	-222.0×10^{-3}
OH^-	-157.3	-230.0	-10.7×10^{-3}

$$\Delta G^{\circ}_{R} = (-157.3) + 3 \times (-1019.0) + 5 \times (-553.5) - (-6338.4) = \quad \text{kJ/mole}$$

$$\Delta H^{\circ}_{R} \quad \text{kJ/mole}$$

$$\Delta S^{\circ}_{R} = \quad \text{kJ/mol K}$$

at T=298.15K (25°C)

$$\Delta G = \Delta H - T \Delta S$$

Is this reactions spontaneous as written?

$-\Delta G^{\circ}_{R}$ means reaction is spontaneous as written

Is the reaction exothermic or endothermic?

$-\Delta H^{\circ}_{R}$ means the reactions is exothermic and heat is given

Does the entropy increase or decrease with this reaction?

$-\Delta S^{\circ}_{R}$ means that there is a decrease in entropy

A quantity closely related to G is the chemical potential (μ), which is defined as:

$$\mu_i = \left(\frac{\Delta G}{\Delta n_i} \right)_{T,P}$$

where,

i refers to a particular component in the system, and

n is the number of moles of that component being added to the system.

The chemical potential μ_i is the partial molar Gibbs free energy or the amount (per mole) by which the Gibbs free energy of the system changes with the addition of an infinitesimal amount of a particular component.

Other quantities related to G include activity a and fugacity f .

Activity a , is considered as an effective concentration (or the thermodynamic concentration) fo liquids and solids, while,

fugacity f is an effective pressure for gases.

You can also think of the activity a of a substance as a fraction of the total concentration that participates in reactions. Typically, activity a is less than the concentration. $a < m$

For solutes in aqueous solutions, the activity approaches its concentration as the concentration of the dissolved solute approaches zero:

$$a_i \rightarrow m_i \text{ as } \sum m_i \rightarrow 0.$$

where, m_i is the molal concentration of component i in the aqueous solution.

The ratio of an activity to a component to its molal (moles of i in 1 kg of water) concentrations is the activity coefficient: (γ), where, $\gamma_i = a_i/m_i$

and hence, $\gamma_i \rightarrow 1$ as $\sum m_i \rightarrow 0$.

Typically, γ is less than 1 for ions and greater than 1 for molecular or neutral species such as $\text{CO}_2(\text{aq})$ and silicic acid (H_4SiO_4).

If always present during a reaction (and always in excess), the activities of pure solids and liquids may be assumed to be unity, or $a_i = 1$.

The chemical potential of component i , can be expressed as :

$$\begin{aligned}\mu_i &= \mu_i^\circ + RT \ln a_i \\ \mu_i &= \mu_i^\circ + RT \ln f_i\end{aligned}$$

where, μ_i° is a constant which is the chemical potential of component i in its standard state,

R is the gas constant (8,314.3 J/mol K; 1.98717 cal/mol K)

T is temperature in Kelvin.

using the expression:

$$\Delta G = n_i u_i$$

we can now have the equation:

$$\Delta G_R = \Delta G_R^\circ + RT \ln \left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \right)$$

We can also write an equilibrium constant (K_{eq}) for the reaction:

$$K_{eq} = a_{\text{products}}/a_{\text{reactants}}$$

$$K_{eq} = \frac{(a_C^c)(a_D^d)}{(a_A^a)(a_B^b)}$$

The equilibrium constant is related to the standard free energy of reaction by the equations:

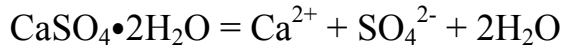
$$\ln K_{eq} = \frac{-\Delta G_R^\circ}{RT}$$

$$\log K_{eq} = \frac{-\Delta G_R^\circ}{2.303RT}$$

$$\log K_{eq} = \frac{-\Delta G_R^\circ}{5.708}$$

at 25°C, and ΔG_R° is in kJ/mol.

Example: Let's calculate the equilibrium constant for the dissociation reaction of gypsum.



$$K_{eq} = \frac{(a_{\text{Ca}^{2+}})(a_{\text{SO}_4^{2-}})(a_{\text{H}_2\text{O}}^2)}{a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}}$$

for dilute solutions, $a_{\text{H}_2\text{O}}$ equals 1

Gypsum is in its standard state as a pure solid, therefore, $a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$ equals 1.

The equilibrium expression above can be reduced to:

$$K_{eq} = (a_{\text{Ca}^{2+}})(a_{\text{SO}_4^{2-}}) = K_{sp}$$

In this example the K_{eq} of the reaction is equal to the K_{sp} (solubility product) of gypsum.

We can calculate what the K_{eq} or K_{sp} for gypsum is by the relationship:

$$\log K_{eq} = \frac{-\Delta G_R^\circ}{5.708}$$

	Gypsum	Ca^{2+}	SO_4^{2-}	H_2O
ΔG_f	-1797.36	-552.8	-744.0	-237.14

$$\Delta G_R = -552.8 + (-744.0) + 2(-237.14) - (-1797.36) = +26.28 \text{ kJ/mol}$$

$$\log K_{eq} = \frac{-26.28}{5.708} = -4.60$$

The equilibrium constant or solubility product for gypsum at 25°C is $10^{-4.60}$. Note in class handouts are tabulated values of $\log K_{eq}$ and ΔH°_R . From this table, the $\log K_{eq}$ for gypsum is listed as = -4.58, which is slightly different than our calculated value of -4.60. The differences between our calculated $\log K_{eq}$ for gypsum using the Gibbs free energy of reaction Appendix II handouts and the $\log K_{eq}$ value given in Appendix III handouts is a common problem of inconsistency existing between thermodynamic data sets. Differences in values between data sets arise from different experimental methods used to measure Gibbs free energy (calorimetry, solubility measurements, or phase equilibrium) as well as experimental uncertainty in determining if a reaction has reached equilibrium. As a rule, it is best to obtain $\log K_{eq}$ values from tables as opposed to calculated from Gibbs free energies. It is also best to get all of your data for an equation from one data set, as opposed to mixing values from various data sets.

We can calculate the solubility product of gypsum at different temperatures using the expressions:

$$\ln K_{eq} = \frac{-\Delta G^\circ_R}{RT}$$

$$\log K_{eq} = \frac{-\Delta G^\circ_R}{2.303RT}$$

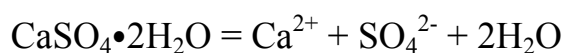
$$\ln K_{eq} = \frac{-\Delta H^\circ_R}{RT} + \frac{\Delta S^\circ_R}{R}$$

$$\ln K_{T_2} - \ln K_{T_1} = \frac{\Delta H^\circ_R}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log K_{T_2} - \log K_{T_1} = \frac{\Delta H^\circ_R}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Use whichever expression fits the information you have.

Example. Estimate the solubility product of gypsum at 40 ° C.



From Appendix III handouts. $\log K_{\text{eq}} = -4.58$, and $\Delta H^\circ_{\text{R}} = -0.46 \text{ kJ/mol}$.

solving the second equation from above

T is in K = °C + 273.15 (at 25°C = 298.15°K)

R = 8.3143 J/mol K or $8.3143 \times 10^{-3} \text{ kJ/mol K}$

$\log K_{40^\circ\text{C, gypsum}} = -4.584$ compared with -4.58 at 25 °C

The solubility of gypsum is about 1% less at 40°C than at 25°C.

Whether the solubility of a mineral increases or decreases with increasing temperature is dependent upon the sign of $\Delta H^\circ_{\text{R}}$.

If $\Delta H^\circ_{\text{R}}$ is positive, the solubility will increase with increasing temp.

If $\Delta H^\circ_{\text{R}}$ is negative, the solubility will decrease with increasing temp.

Measurements of Disequilibrium

$$K_{eq} = \frac{(aC^c)(aD^d)}{(aA^a)(aB^b)}$$

The right hand side of this equation is called the *ion activity product* (IAP).

For a system at equilibrium, $IAP = K_{eq}$

For a system out of equilibrium $IAP \neq K_{eq}$.

can also be expressed as IAP/K_{eq} where

$IAP/K_{eq} = 1$ at equilibrium

$IAP/K_{eq} < 1$ the reaction will proceed to the right

$IAP/K_{eq} > 1$ the reaction will proceed to the left

Another useful concept is the comparing the IAP to the K_{sp} of a mineral.

If the $IAP > K_{sp}$, solution is *oversaturated*, and the mineral is expected to precipitate out of the solution.

If the $IAP < K_{sp}$, solution is *undersaturated*, and the mineral is expected to dissolve into the solution.

Often we use the term *saturation index* (SI), where

$$SI = \log(IAP/K_{sp})$$

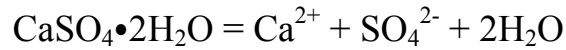
In this expression,

$SI < 0$ for undersaturation

$SI > 0$ for oversaturation

Example:

Estimate the saturation state with respect to gypsum of a water sample that has a calcium activity of $10^{-3.5}$ and sulfate activity of $10^{-1.5}$.



$$K_{eq} = \frac{(a\text{Ca}^{2+})(a\text{SO}_4^{2-})(a^2\text{H}_2\text{O})}{a\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$$

$$K_{eq} = (a\text{Ca}^{2+})(a\text{SO}_4^{2-}) = K_{sp}$$

$$\text{IAP} = (a\text{Ca}^{2+})(a\text{SO}_4^{2-}) = 10^{-3.5} \times 10^{-1.5} = 10^{-5.0}$$

From Appendix III, $K_{sp} = 10^{-4.58}$, for gypsum.

$$\text{IAP} < K_{sp}, 10^{-5.0} < 10^{-4.58}$$

Therefore, the solution is undersaturated with respect to gypsum.

$$\text{If we take the } \log(\text{IAP}/K_{sp}) = \log(10^{-5.0}/10^{-4.58}) = \log 10^{-0.42} = -0.42$$

The SI = -0.42, is negative and therefore undersaturated.

SI close to zero, say plus or minus 0.05 are considered to be at equilibrium.

SI values far from equilibrium have SI values of plus or minus 1.0 or greater.