Lecture 3

A. Partition Coefficient (read “Terminology for trace-element partitioning”, Beattie et al., Geochim. Cosmochim. Acta, 57, 1603-1606, 1993)). The partition coefficient is the concentration ratio of an element (i) between two phases (α and β) is

\[ D_{i}^{\alpha/\beta} = \frac{C_{i}^{\alpha}}{C_{i}^{\beta}} \]

Within the region of Henry’s Law behavior, the partition coefficient is independent of the concentration of “i” but it is dependent on temperature, pressure and phase composition.

Nomenclature: for applications to igneous rocks where partitioning of elements between solid phases (s) and melt (ℓ) are important, most papers follow the convention of

\[ D_{i}^{s/\ell} = \frac{C_{i}^{s}}{C_{i}^{\ell}} \]

(D_{i}^{s/\ell}) the partition coefficient is also known as the distribution coefficient).

Note that D is commonly used for partition coefficient but if kinetic considerations are combined with studies of trace element partitioning, D has precedence for designating Diffusion Coefficient. Also K designates equilibrium constant, and K_D or K_C are used to designate compound partition coefficients. A common example is \( K_{D}^{Fe/Mg} = \frac{(Fe/Mg)_{olivine}}{(Fe/Mg)_{melt}} \); that is, K_D or K_C are ratios of two partition coefficients.
B. Relationship between partition coefficient and equilibrium constant

Consider partitioning of Ni between forsterite solid (Mg$_2$SiO$_4$) and a melt of the same composition:

\[ K_{eq} = \frac{a_{Ni}^s}{a_{Ni}^\ell} = \frac{x_{Ni}^s \gamma_{Ni}^s}{x_{Ni}^\ell \gamma_{Ni}^\ell} \]

Therefore \( D = \frac{x_{Ni}^s}{x_{Ni}^\ell} = K_{eq} \left( \frac{\gamma_{Ni}^\ell}{\gamma_{Ni}^s} \right) \)

i.e., the partition coefficient is related to the equilibrium constant by a ratio of activity coefficients (\( \gamma \)).

C. Formation Reaction

The partitioning of Ni between Mg$_2$SiO$_4$ solid and melt can also be described by a formation reaction (see Wood and Fraser, Chapter 6).

\[ 2NiO(l) + SiO_2(l) = Ni_2SiO_4(s) \]

\[ K_{eq} = \frac{a_{Ni_2SiO_4}^{\ell}}{(a_{NiO})^2(a_{SiO_2}^\ell)} = \frac{(\gamma_{Ni_2SiO_4}^{\ell})(x_{Ni_2SiO_4}^{\ell})}{(\gamma_{NiO}x_{NiO}^{\ell})^2a_{SiO_2}^\ell} \]

Since \( D = \frac{x_{Ni_2SiO_4}^{\ell}}{x_{NiO}^\ell} \) it is clear that D is sensitive to \( a_{SiO_2}^\ell \).

(We will see later that mineral/melt D’s vary with the SiO$_2$ content of melts).

D. Exchange Reaction

The same partitioning process can be described by

\[ 2MgO(l) + Ni_2SiO_4(s) = 2NiO_{(l)} + Mg_2SiO_4(s) \]

\[ K_{eq} = \frac{(a_{NiO}^\ell)^2(a_{Mg_2SiO_4})}{(a_{MgO}^\ell)^2(a_{Ni_2SiO_4}^s)} \]

and
\[ K_{eq} = \frac{(\frac{\gamma_{NiO}}{\gamma_{MgO}})^2}{(\frac{\gamma_{Ni_2SiO_4}}{\gamma_{Mg_2SiO_4}})} \times \frac{(\frac{x_{NiO}}{x_{MgO}})^2}{(\frac{x_{Ni_2SiO_4}}{x_{Mg_2SiO_4}})} \]

This is a compound partition coefficient involving the ratio of two partition coefficients (Ni and Mg), i.e. \( K_D = (X_{Mg_2SiO_4}/X_{Ni_2SiO_4}) / (X_{MgO}/X_{NiO}) \) so that \( K_{eq} = K_D \) times a ratio of activity coefficients. If Ni and Mg are non-ideal to similar extents, it might be expected that the ratio of activity coefficients for NiO/MgO is near unity. As a result \( K_D \) may be more nearly constant than \( D \). Also note that the \( a_{SiO_2}^f \) term has cancelled out.

**E. Geothermometer/Geobarometer**

Since equilibrium constants vary with pressure and temperature, partition coefficients are also a function of pressure and temperature; hence there is the potential of using variations in TE partition coefficients to infer \( P \) and \( T \).

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \Delta U^\circ + P\Delta V^\circ - T\Delta S^\circ = -RT\ln K_{eq} \]

So

\[ \ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

\[ (\frac{\partial \ln K_{eq}}{\partial T})_P = \frac{\Delta H}{RT^2} \] or

\[ (\frac{\partial \ln K_{eq}}{\partial 1/T})_P = -\frac{\Delta H^\circ}{R} \] so

a plot of \( \ln K_{eq} \) (lnD) versus \( 1/T \) yields a straight line. Similarly a geobarometer for pressure is

\[ (\frac{\delta \ln K}{\delta P})_T = \frac{-\Delta V^\circ}{RT} \]
(relatively little is known about D variations versus pressure).