

ESS 312 Geochemistry Introduction to Thermodynamics

Concepts and definitions you need to understand:

(i) We use (equilibrium) thermodynamics:

- to predict the stable state of a system under specified conditions (P, T and composition), or ...
- to infer from the preserved state of a system the conditions under which it formed.

(ii) We will generally specify a *system* by its composition - numbers of moles of defined chemical *components*. Note that we don't have to choose components that are pure elements (Si, O, Al, etc). It may be simpler to choose building blocks such as (SiO₂, Al₂O₃), as long as all the *phases* that may form in the system can be represented as reaction products of the chosen components. Each chemically distinct substance that forms in the system is called a "*phase*". The phases of interest in geochemical systems are minerals, melts (silicate liquids), fluids (usually aqueous) and gases.

(iii) To describe a thermodynamic system we need to specify or calculate *conditions*: Pressure (P), Temperature (T) and the chemical potential of each component (μ_i), and *properties*: Internal Energy (U), Entropy (S), Volume (V) and composition - the number of moles (n_i) of each chemical component in the system. Notice that the first three describe the "condition" of the system, the latter three describe the "extent" of the system. These are "*intensive*" and "*extensive*" variables, respectively.

(iv) Many of the problems we confront will involve predicting the stable state of a system, which we refer to as the state of *chemical equilibrium*. This is another way of asking which possible *transformations* of the system (i.e. chemical reactions) will occur *spontaneously* to achieve equilibrium.

(v) We use a family of *thermodynamic potentials* to decide which processes will occur spontaneously. Just as gravitational potential energy relative to the ground (the stable state toward which an object falls) measures how far the object is from stability, thermodynamic potentials like the *Gibbs Free Energy* (G), or the *Enthalpy* (H) indicate how far a system is from equilibrium and whether it will *transform spontaneously* to attain equilibrium.

(vi) Based on the principle of the conservation of energy, and the consideration that, in a spontaneous ("irreversible") process, heat transferred to the system increases its entropy such that $dS \geq dq/T$, we derived the condition for deciding whether a transformation will occur *spontaneously*. If the process results in changes in the internal energy, entropy and volume of the system such that:

$$dU - T dS + P dV \leq 0,$$

then it will occur spontaneously.

(vi) Given this criterion, it makes sense to postulate a *potential* called the *Gibbs Free Energy* (G), which we can use to determine the equilibrium state of systems in which P and T are regulated externally (i.e. in which the transformations that may take place will not affect the pressure and temperature of the

$$G = U - TS + PV,$$

Notice that as long as P and T are fixed externally (hence $dP = 0$ and $dT = 0$), then a small change in G can be expanded into the following expression:

$$\begin{aligned} dG &= dU - T dS - S dT + P dV + V dP, \\ &= dU - T dS + P dV, \end{aligned}$$

and therefore that $dG \leq 0$ for spontaneous transformations (from the criterion above).

- (vii) It is vital to understand that we can calculate G (in units of kJ/mol) for any substance at any chosen P and T. For example, in the simple, single-component system Al_2SiO_5 , there are three possible phases, the minerals andalusite, kyanite, sillimanite. We can calculate a Gibbs Free Energy value for each of these at every possible combination of P and T. We find that at low P and T, the Gibbs Free Energy of andalusite is lowest. Conversely, at low P and high T we find that sillimanite has the lowest Gibbs Free Energy. This tells us that if we subject andalusite to sufficiently high T, keeping pressure low, it will transform spontaneously to sillimanite, thereby lowering the Gibbs Free Energy of the system. (At low T and high P, G_{kyanite} is lower than $G_{\text{andalusite}}$ and $G_{\text{sillimanite}}$, so kyanite is the stable phase).
- (viii) This is the same as writing chemical reactions describing possible transformations between the phases in a system (e.g. andalusite \rightarrow sillimanite, in the simple system above). For each possible transformation we can calculate a *change in Gibbs Free Energy*:

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

and if $\Delta G \leq 0$, the transformation will occur spontaneously. Do not confuse G and ΔG . ΔG only has meaning once you have written a reaction. For a reaction involving several reactant phases and several product phases, G_{products} and $G_{\text{reactants}}$ are determined by adding up the G values of the participants on each side of the reaction. The reaction proceeds in whichever direction leads to the phase assemblage with lower Gibbs Free Energy.

- (ix) Values for G cannot be measured in an absolute sense. Instead we define the "Gibbs Free Energy of Formation" (G_f^0) of a compound at a standard temperature of 298.16K and 1 atm pressure and calculate values of G relative to this. We will discuss how to calculate G values away from standard temperature and pressure in lectures and lab. Pure elements in their standard states at 298.16K and 1 atm pressure (e.g. graphite, metallic iron, fluorine gas) are assigned G_f^0 values of zero.