

## 12.480

### A brief review of the thermodynamics of solutions

**Equilibrium** A system or phase is in equilibrium, if its physical properties do not change with time.

*Homogeneous Equilibrium* Refers to equilibrium within a single phase.

*Heterogeneous Equilibrium* Refers to equilibrium involving several phases.

**State** The state of matter is defined by its intensive physical properties.

**Intensive properties** A property that is independent of the extent or bulk of a system or phase. The value for the property for the entire phase is the same as it is for each part. Pressure, temperature, density and chemical potential ( $\mu$ ) are intensive properties.

**Extensive Properties** A property whose value depends on the extent or amount of the system or phase. Examples are volume and mass (or number of moles), energy and entropy.

**Equations of State** Analytical expressions that allow prediction of various functions of state. These can be used to predict direction of reaction and energetics of phase transitions.

**Phase** A physically homogeneous substance.

**Phase Region or Solution or Solid Solution** Physically homogeneous substances belong to a phase region if a continuous series of phases can be made that span the gap between the substances. Gases and liquids often form solutions. Many solid earth materials also are solutions.

In thermodynamics, the “laws” are essentially a methodology for keeping track of the way in which the the various state functions change in a substance.

**1st law of thermodynamics** The first law is a statement of equivalence of thermal and mechanical energy. The mechanical work ( $W$ ) performed bears a predictable relationship to the heat produced ( $q$ ):

**2nd law** There are changes in nature that have a definite sense. Entropy (disorder) is the state function that deals with one of these, and the second law relates to the irreversibility inherent in change of this state function.

$$kdq \geq dW$$

**Energy functions** These are state functions that can be used to indicate the direction of change. Our introductory thermodynamics classes usually bring us up to the point of

dealing with equilibrium in “closed” systems, where no mass transfer takes place. The combined statements of the first and second law relates to this change of heat and work:

$$dE \leq TdS - PdV.$$

There is nothing in this statement that can deal with the change in energy associated with a change in the mass or amount of a phase. In order to deal with equilibria in multi-component multi-phase materials, we must consider the change in energy associated with a change in mass. In the case of E (internal energy) this energy change is defined as the chemical potential.

$$\left( \frac{\partial E}{\partial n_i} \right)_{S, V, n_j \neq n_i}$$

In particular, G - the Gibbs Free energy - and its related variable  $\mu$  - the chemical potential - are useful in understanding equilibria in earth materials.

G - Gibbs free energy measures the changes in energy of a system in terms of changes in T, P and n (the mass of a phase). The chemical potential  $\mu$  in component  $i$  is the change in Gibbs free energy function associated with a change in mass in the phase

$$\mu_i = \left( \frac{\partial G_i}{\partial n_i} \right)_{T, P, n_j \neq n_i}$$

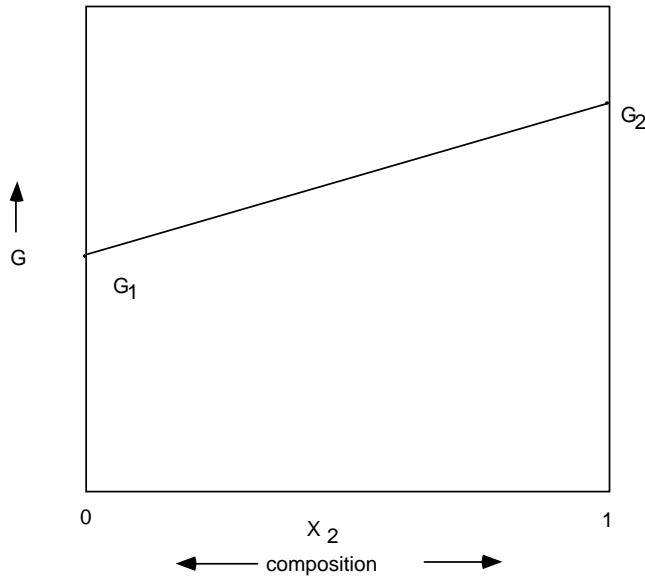
By measuring the chemical potential of a phase, one can determine the tendency of a phase to react or change mass. The direction of change is from high chemical potential to low chemical potential. The energy of the system as a whole is minimized at equilibrium.

## The existence of solutions in liquids and crystals

Recall our statement that the equilibrium state was the one with the lowest free energy. A solution exists when you mix two things together and the result is a spontaneous and irreversible decrease in free energy.

(1.) Mechanical mixing. You can do this with a spoon, and undo it if you have the patience. We did it in class with oil and water.

$$G_{\text{system}} = \text{sum of } G\text{'s of the parts or } G = \sum_{j=1,n} n_j \cdot G_j$$



In 2 component systems

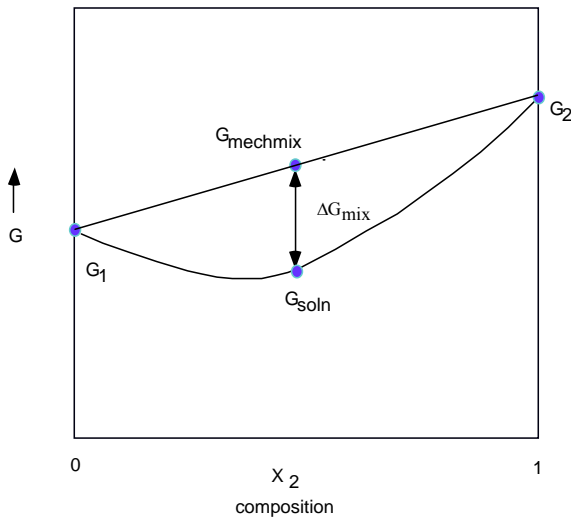
$$G_{\text{mechmix}} = G_1 + X_2(G_2 - G_1)$$

In this instance we are dealing with two separate phases. There is no solution.

(2.) Existence of a solution:

At equilibrium the Gibbs free energy will be minimized. The existence of a solution implies that:

$$G_{\text{soln}} < G_{\text{mechmix}}$$



$$\Delta G_{\text{mix}} = G_{\text{soln}} - G_{\text{mech mix}}$$

This concave upward curve also implies that any mixture of nearby solns. has a higher free energy and is unstable with respect to a solution

intermediate to A & B.

Gibbs Free Energy of Mixing.

$$G_{\text{soln}} = \sum_{i=1,n} X_i G_i + \Delta G_{\text{mix}}$$

$$\text{where } \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

### Ideal solution

By definition, an ideal solution is one in which:

$$\Delta H_{\text{mix}} = 0$$

and

$$\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}}$$

It is a solution for which the only contribution to  $G_{\text{mix}}$  is from entropy of mixing. An ideal solution is one which obeys Raoult's Law.

### Estimation of Free Energy of Mixing in an Ideal Solution.

A statistical analog of entropy of mixing can be formulated by considering the probability of finding the system in a particular state A characterized by a particular energy  $E_A$ .  $P_A$  is the probability of the system being in this state.  $P_A$  is related to the # of ways of arranging things so that state A with energy  $E_A$  can be achieved.

If  $W_A = \#$  of arrangements that result in state A,  
then  $P_A$  is related to  $W_A$ .

The most probable state is, naturally, the equilibrium state.

The solution is made up of several/many particles, and each particle can exist in several states. Probability is multiplicative, and the probability of finding state A is the probability of finding particle 1 in state A, particle 2 in state A, particle 3 in state A, etc.

$$P_A = P_{1A} \cdot P_{2A} \cdot P_{3A} \dots \text{etc.}$$

and

$$W_A = W_{1A} \cdot W_{2A} \cdot W_{3A} \dots \text{etc.}$$

Entropy is an extensive property

$$S_{\text{total}} = S_1 + S_2 + S_3 \dots \text{etc.}$$

$$\text{and } S_{\text{total}} = f(W_{1A} + W_{2A} + W_{3A} \dots \text{etc.})$$

To relate the additive property (entropy) and the multiplicative property (probability) requires the use of the log function.

$$\text{since } \ln W_A = \ln W_{1A} + \ln W_{2A} + \ln W_{3A} \dots$$

$$S = k \ln W + b \quad (\text{k is a proportionality constant, the Boltzman constant})$$

Consider the number of ways that some fraction of the atoms in a crystalline solution can be arranged on n sites per gram formula of a crystal.

$$nN = \# \text{ of sites, where } N \text{ is Avogadro's number and } n \text{ is the } \# \text{ of sites per gram formula unit.}$$

$x$  = mole fraction of a particular site filled with the atom.

We want to know the # of ways ( $W$ ) that  $xnN$  atoms occupy the  $nN$  sites.

This is given by the combinatorial formula:

$$W = (nN)! / [ (xnN)! \cdot (nN-xnN)! ]$$

$$\ln W = \ln (nN)! - \ln (xnN)! - \ln (nN-xnN)!$$

We apply Stirling's approximation for logarithms of large numbers,

$$\ln N! = N \ln N - N$$

and plug in

$$\ln W = -nN[x \ln x + (1-x) \ln(1-x)]$$

Thus, for Entropy:

$$\Delta S_{\text{mix}} = -knN[x \ln x + (1-x) \ln(1-x)]$$

This is the Entropy value for mixing  $xnN$  atoms on  $nN$  sites.  
 $R = k N$ , where  $k$  is Boltzmann's constant &  $N$  is Avogadro's #.

$$\Delta S_{\text{mix}} = -nR[x \ln x + (1-x) \ln(1-x)]$$