

## Notes 9: Thermodynamics (3)

### VIII. Equilibrium constants

### IX. Activity

### X. P, T, and K

Phases that are not pure:

liquid solutions

solid solutions

gaseous solutions

#### The Law of Mass Action for Ideal Gases

$$dG = VdP - SdT$$

Ideal gas: gas that obeys the following equation of state:  $PV = nRT$  or per mole of ideal gas:  $PV = RT$ .

Imagine a process whereby an ideal gas is diluted at constant total  $P$  and constant  $T$ , from a pure gas.

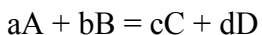
$$dG = VdP$$

$$\int_{G^\circ(P,T)}^{G(P_p,T)} dG = \int_P^{P_p} V dP$$

$$\int_{G^\circ(P,T)}^{G(P_p,T)} dG = \int_P^{P_p} RT dP/P$$

$$G(P_p, T) - G^\circ(P, T) = RT \ln P_p/P$$

Imagine that you have 4 ideal gases that participate in the following reaction:



Then:

$$\Delta G_R - \Delta G^\circ_R = RT \{ \sum n_i \ln P_i/P \text{ (products)} - \sum n_j \ln P_j/P \text{ (reactants)} \}$$

$$\Delta G_R - \Delta G^\circ_R = RT \{ c \ln P_C/P + d \ln P_D/P - a \ln P_A/P - b \ln P_B/P \}$$

$$\Delta G_R - \Delta G^\circ_R = RT \ln \{ [(P_C/P)^c (P_D/P)^d] / [(P_A/P)^a (P_B/P)^b] \}$$

at equilibrium  $[(P_C/P)^c (P_D/P)^d] / [(P_A/P)^a (P_B/P)^b] = K$  and  $\Delta G_R = 0$

$$\Delta G^\circ_R = -RT \ln K$$

## Law of Mass Action for real gases, liquids, and solids

fugacity =  $f$ : effective pressure. The pressure a real gas would have if it were an ideal gas - must measure  $V$  as a function of  $P$  and  $T$  for each real gas to get fugacity.

$f = \gamma P$ , where in this case  $\gamma$  is the fugacity coefficient, which must be measured as a function of  $P$  and  $T$  for each real gas.

For real gas:  $K = [(f_C/f^\circ)^c (f_D/f^\circ)^d] / [(f_A/f^\circ)^a (f_B/f^\circ)^b]$

$f^\circ$  = standard state fugacity. A number of possibilities can be chosen for the standard state. A different standard state can be chosen for different compounds in a reaction.

activity is usually denoted "a" and  $a = f/f^\circ$

mole fraction is denoted "X" and is the number of moles of one end member of a solid solution divided by the total number of moles in the solid solution. Each "X" is specific to a particular endmember and can have values between 0 and 1.

$f^\circ$  may be defined as:

- (1) fugacity of a gas in equilibrium with a pure solid at the temperature and pressure of interest. In this case  $a = X$  for  $X \approx 1$  (most solids, solvents)
- (2) hypothetical fugacity chosen so that  $a = X$  at small  $X$  (solids components that are typically present in small amounts - trace metals)
- (3) hypothetical fugacity chosen so that  $a = m$  at small  $m$  (solute)

$a = \gamma X$  or  $a = \gamma m$ , depending of which  $f^\circ$  is chosen, where  $\gamma$  in this case is called the activity coefficient, and again must be determined empirically.

In terms of activity:

$$K = [a_C^c a_D^d] / [a_A^a a_B^b].$$

If  $\gamma = 1$ , the solution, whether solid or liquid, is said to be "ideal" and the activities in the above equation can be replaced by either  $X$  or  $m$  or some combination of the two depending on how the  $f^\circ$  is defined.

For example if a reaction involves only ideal solutions for which the  $a = X$  at  $X = 1$  standard state is chosen, then:

$$K = [X_C^c X_D^d] / [X_A^a X_B^b].$$

Combining the Law of Mass Action with the equation relating change in Free Energies of pure substances with pressure and temperature

$$\Delta G_R(P, T) - \Delta G^\circ_R(P, T) = RT \ln K$$

For solid-solid reactions:

$$\Delta G^\circ_R(P, T) - \Delta G^\circ_R(P_1, T_1) \approx \Delta V_R(P - P_1) - \Delta S_R(T - T_1)$$

Substituting, we get:

$$\Delta G_R(P, T) - \Delta V_R(P - P_1) + \Delta S_R(T - T_1) - \Delta G^\circ_R(P_1, T_1) \approx RT \ln K$$

setting  $\Delta G_R(P, T)$  to zero, as must be the case at equilibrium, and solving for P:

$$P \approx [(\Delta S_R - R \ln K) / \Delta V_R] T - (\Delta S_R / \Delta V_R) T_1 + P_1 - \Delta G^\circ_R(P_1, T_1) / \Delta V_R$$

(as compared to the analogous equation derived earlier for pure substances:

$$P \approx (\Delta S_R / \Delta V_R)(T) - (\Delta S_R / \Delta V_R)T_1 + P_1 - \Delta G^\circ_R(P_1, T_1) / \Delta V_R$$