

## Practical 2: Thermodynamic Calculations (SOLUTIONS)

### Background: Gibbs Free Energy of a Chemical Reaction

As you will learn in the next few lectures, the Gibbs free energy ( $G$ ) of a substance at a temperature  $T$  (in K) given by

$$G = H - TS$$

where  $H$  is the enthalpy and  $S$  is the entropy. In practice, we take  $H$  to be that required for the *formation of the substance from the elements* (designated  $\Delta H_f$ ) (This means that the  $\Delta H_f$  for any pure element is simply zero.). For a chemical reaction from  $A$  to  $B$ , the change in  $G$ ,  $\Delta G$ , will be

$$\Delta G = (\Delta H_f^B - \Delta H_f^A) - T(S^B - S^A) = \Delta H - T\Delta S$$

The problem is that  $H$  and  $S$  are functions of pressure ( $P$ ) and temperature ( $T$ ). A pretty good approximation (valid when the change in heat capacity between products and reactants,  $\Delta C_p = 0$ ) is that

$$\Delta G(P, T) = \Delta H(P_0, T_0) - T\Delta S(P_0, T_0) + \int_1^P \Delta V dP$$

where  $\Delta H(P_0, T_0)$  means  $\Delta H$  when  $P=P_0$  and  $T=T_0$ .  $P_0$  is usually 1 bar and  $T_0 = 298$  K.

### Part I: Equilibria Between Pure Solid Phases

Most minerals are not very compressible; over the pressure range of the Earth's crust, the molar volume of a mineral is nearly constant. If the reaction involves only mineral (solid) phases, then to a good approximation  $\Delta V$  is constant. When that's true, the integral is very easy:

$$\Delta G = \Delta H_{1bar} - T\Delta S + (P - P_0)\Delta V$$

where  $\Delta V$  is the molar volume change of the reaction. If two substances  $A$  and  $B$  are in *chemical equilibrium*, then the difference in free energy between them will be zero:

$$\Delta G = \Delta H_{1bar} - T\Delta S + (P - P_0)\Delta V = 0$$

we can use this to calculate the boundary in P,T space between two phases.  
Along this boundary, both phases will coexist.

**1. Using the approximation that the P,T phase boundary is defined by  $\Delta H_{1\text{bar}, 298\text{K}} - T\Delta S_{298\text{K}} + (P-P_0)\Delta V = 0$ , calculate the phase diagram (plot P vs T) for calcite-aragonite given the following thermodynamic data: (Be careful! Use the unit factor method to convert  $(P-P_0)\Delta V$  into kJ/mole.)**

Species	$\Delta H_{f, 1\text{bar}}$ (kJ/mol)	$S_{298\text{K}}$ (kJ/mol-K)	V (cm <sup>3</sup> /mole)
Calcite, CaCO <sub>3</sub>	-1207.37	0.09171	36.93
Aragonite, CaCO <sub>3</sub>	-1207.43	0.08799	34.15

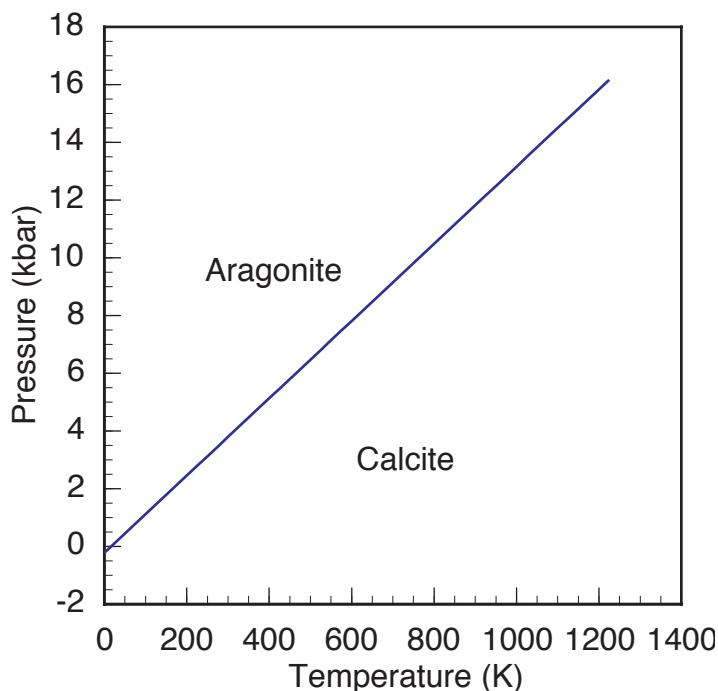
Solution: For the reaction Calcite = Aragonite:

$$\begin{aligned}\Delta H &= -1207.43 - (-1207.37) = -0.06 \text{ kJ/mole} \\ \Delta S &= 0.08799 - 0.09171 = -0.00372 \text{ kJ/mol-K} \\ \Delta V &= 34.15 - 36.93 = -2.78 \text{ cm}^3/\text{mole}\end{aligned}$$

Thus

$$\begin{aligned}\Delta G &= -0.06 \text{ (kJ/mole)} - T(\text{K})(-0.00372) \text{ kJ/mol-K} \\ &\quad + (P-P_0)(-2.78 \text{ cm}^3/\text{mole})(10^{-4} \text{ kJ/bar-cm}^3) \\ &= -0.06 + 0.00372T - (2.78 \times 10^{-4})(P) + 2.78 \times 10^{-4} = 0\end{aligned}$$

$$\text{or } P \text{ (bar)} = -214.8 + 13.4T$$



## Part II: Equilibria involving gas phases

Gases are very compressible. If a chemical reaction involves a gas phase, then  $\Delta V$  will be a strong function of pressure. Hence we will not be able to make the approximation

$$\int_{P_0}^P \Delta V dP = (P - P_0) \Delta V.$$

Instead, we need an *equation of state* to evaluate  $\Delta V$  as a function of pressure. We can use the ideal gas law,  $PV = nRT$ , as a first approximation. For a reaction  $A(\text{solid}) = B(\text{solid}) + C(\text{gas})$ ,  $\Delta V = V_C + V_B - V_A \approx V_C$  (the volume change of the solids is much smaller than that of the gas)

$$\int_{P_0}^P \Delta V dP \approx \int_{P_0}^P V_{\text{gas}} dP = \int_{P_0}^P \frac{nRT}{P} dP = nRT \ln\left(\frac{P}{P_0}\right)$$

**2. Calculate the phase diagram for the dehydration of brucite  $\text{Mg}(\text{OH})_2$  to periclase  $\text{MgO}$  and  $\text{H}_2\text{O}(\text{gas})$  given the following thermodynamic data.**

(Assume steam is an ideal gas; do we need to include the volume change of the solids?)

Species	$\Delta H_f, 1\text{bar}$ (kJ/mol)	<b>S</b> (kJ/mol-K)	<b>V</b> ( $\text{cm}^3/\text{mole}$ )
Brucite ( $\text{Mg}(\text{OH})_2$ )	-924.54	0.06318	24.63
Periclase ( $\text{MgO}$ )	-601.49	0.02694	11.25
Steam ( $\text{H}_2\text{O}$ )	-241.81	0.18872	24789.2

Solution:

For the reaction  $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}(\text{g})$

$$\Delta H = -241.81 - 601.49 - (-924.54) = 81.24 \text{ kJ/mole}$$

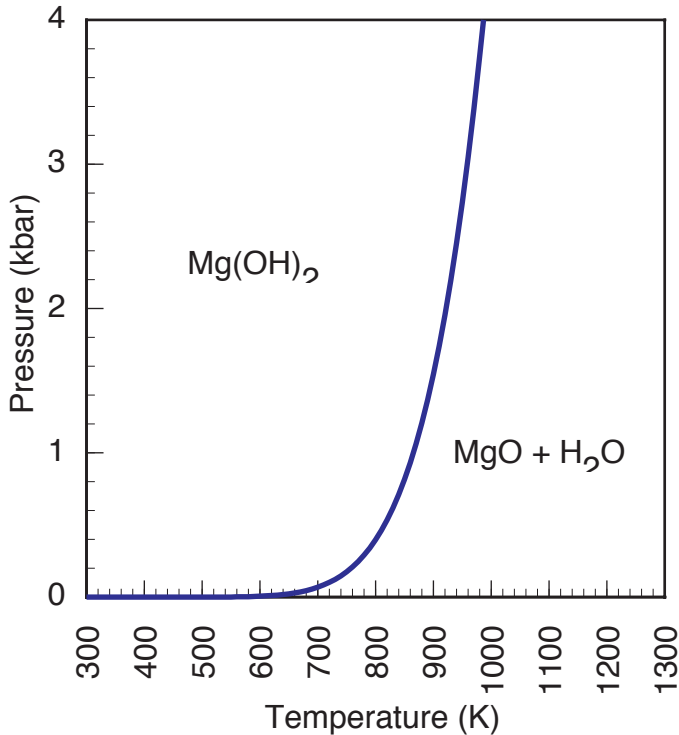
$$\Delta S = 0.18872 + 0.02694 - 0.06318 = 0.1525 \text{ kJ/mol-K}$$

$$\begin{aligned} \int_1^P \Delta V dP &\approx \int_1^P V_{\text{gas}} dP = \int_1^P \frac{nRT}{P} dP = nRT \ln\left(\frac{P}{1}\right) \\ &= 0.00831 \left( \frac{\text{kJ}}{\text{mol-K}} \right) T(\text{K}) \ln\left( \frac{P \text{ bars}}{1 \text{ bar}} \right) \end{aligned}$$

Thus, along the reaction boundary:

$$\Delta G = 81.24 - T(0.1525) + 0.00831T(\ln(P)) = 0$$

$$\text{or } P \text{ (bar)} = \text{Exp}(-9771/T + 18.2)$$



### Part III: Equilibria Involving Mixtures

In the two previous problems, the products and reactants were all separate pure *phases*. Many problems in geochemistry involve phases that are mixtures of several *components*. An example is an aqueous solution (e.g., 1 mole of NaCl in water) or a solid solution between two endmembers (e.g., forsterite,  $\text{Mg}_2\text{SiO}_4$ , and fayalite,  $\text{Fe}_2\text{SiO}_4$  in olivine). As we will derive in the next few lectures, the free energy of a solution is defined in terms of the *activities* of the components. For now, accept the following rules:

- 1) the activity of an ion in aqueous solution is numerically equal to its *molal* concentration (= moles/kg of water). The standard state is 1 molal with the properties of infinite dilution (!).
- 2) The activity of a gas phase component is numerically equal to its partial pressure. The standard state is pure gas component at 1 bar pressure.
- 3) The activity of a pure solid substance is 1.
- 4) The activity of a component in a solid solution is a bit more complicated...

For a chemical equilibrium  $aA + bB = cC + dD$ , we can write an equilibrium constant

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [A] is the activity of A etc. We will show in lecture that  $\ln(K) = -\Delta G^0/RT$ . where  $\Delta G^0$  is the free energy difference between products and reactants when all of the products and reactants are in their standard state (activity = 1).

**3. Given the following thermodynamic data, calculate the equilibrium constant for the dissolution of galena, PbS, at 298 K and 1 bar according to the reaction  $\text{PbS}(\text{solid}) + \text{H}^+ = \text{Pb}^{2+}(\text{aq}) + \text{HS}^-$ . From this, can you calculate the solubility of PbS at pH = 2? (Hint: assume  $[\text{Pb}^{2+}] = [\text{HS}^-]$  and note that  $[\text{PbS}] = 1$  for pure galena; at pH = 2,  $[\text{H}^+] = 0.01$ ).**

Species	$\Delta H_f, 1\text{bar}$ (kJ/mol)	S (kJ/mol-K)
Galena (PbS, solid)	-97.7	0.091
H <sup>+</sup> (aqueous ion, 1 molal)	0.00	0.00
Pb <sup>2+</sup> (aq. ion, 1 molal)	-1.70	0.01
HS <sup>-</sup> (aq. ion, 1 molal)	-17.0	0.063

Solution:

For the reaction  $\text{PbS} + \text{H}^+ = \text{Pb}^{2+} + \text{HS}^-$  we have

$$\Delta H^0 = -17.0 - 1.7 - (0.00 - 97.7) = 79.0 \text{ kJ/mole}$$

$$\Delta S^0 = 0.063 + 0.01 - (0.0 + 0.091) = -0.018 \text{ kJ/mole-K}$$

$$\Delta G^0 = 79.0 - (298)(-0.018) = 84.4 \text{ kJ/mole}$$

$$\ln(K) = -\Delta G/RT = -34.1 \text{ or } \log K = -14.78$$

At pH=2  $[\text{H}] = 0.01$  (also,  $[\text{PbS}] = 1$  and  $[\text{Pb}] = [\text{HS}^-] = x$ )

$$K = \frac{[\text{Pb}^{2+}][\text{HS}^-]}{[\text{PbS}][\text{H}^+]} = \frac{x^2}{0.01} = 1.6 \times 10^{-15}$$

$$x = [\text{Pb}] = 4.0 \times 10^{-9} \text{ moles/kg-water}$$

3. Now calculate the effect of temperature on the  $\log(K)$  for the dissolution of galena at pH 2. Plot  $\log[Pb]$  vs  $T$ . Is PbS very soluble at any  $T$ ? How do we form ore deposits of PbS?

$$2.303\log(K) = \ln(K) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\log(K) = \left(\frac{1}{2.303}\right)\left(\frac{-79.0}{0.00831T} + \frac{-0.018}{0.00831}\right) = \frac{-4128.0}{T} - 0.940$$

$$\log(K) = 2\log[Pb] + pH$$

$$\log[Pb] = \frac{1}{2}(\log(K) - pH) = \frac{-2064.0}{T} - 1.47$$

