10.40 Thermodynamics **Fall 2003**
Final Exam

Problem 4

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4. (20 points) Important reactions between natural minerals occur under high pressure conditions in deep underground reservoirs in the presence of water. For many geologic systems the time scales are so long (typically years to centuries) that equilibrium can be safely assumed. One such system is the gypsum-anhydrite-water equilibrium where

$$\underset{(\text{gypsum})}{CaSO_4 \cdot 2H_2O_{(s)}} = \underset{(\text{anhydrite})}{CaSO_{4\,(s)}} + \underset{(\text{water})}{2H_2O_{(f)}}$$

In deriving the criteria for phase equilibrium, we found that the temperature and pressure of all phases were equal. In deeply located mineral systems in rock reservoirs, fluid phase pressures can be different than solid phase pressures if the rock column above the minerals is permeable to fluid. In other words, the hydraulic gradient and lithostatic gradient of pressure can be different. In this case, the system has one more degree of freedom and the equilibrium distribution of products and reactants at any particular depth depends on fluid pressure (P_f) and solid phase pressure (P_s) where both can be expressed as a function of depth z.

$$P_f = \int_o^z \rho_f g dz \quad \text{(hydraulic)}$$

$$P_s = \int_o^z \rho_s g dz \quad \text{(lithostatic)}$$

For the gypsum-anhydrite system, let's consider what happens over a range of conditions. The standard Gibbs free energy change for the reaction is given by Eq. (8-165):

$$\Delta G^o_{rx}(298\,\text{K}, 1\,\text{bar}) = \sum_{i=1}^{n} v_i \Delta G^o_{f,i}$$

Compound	$\Delta G^o_{f,i}$ **(kJ/mol)**
water H_2O (liquid)	-237.141
gypsum $CaSO_4 \cdot 2H_2O$ (solid)	-1797.20
anhydrite $CaSO_4$ (solid)	-1321.70

Reference states for all components are taken to be unit fugacity at 298 K, 1 bar pressure. The molar volume change for the solid phase gypsum to anhydrite transformation is:

$$\Delta V_{\text{gypsum}\to\text{anhydrite}} = V_{(\text{CaSO}_4)} - V_{(\text{CaSO}_4\bullet 2\text{H}_2\text{O})} = -29.48\,\text{cm}^3/\text{mol}$$

and

$$V_{\text{H}_2\text{O, liquid}} = 18.07\ \text{cm}^3/\text{mol}$$

Over accessible depths, pressures ranged from 1 bar to as high as 1000 bar while temperatures can range from near ambient to 200°C.

(a) (10 points) Assuming that the standard state is now redefined at the temperature and pressure of the system, how will ΔG_{rx}^{o} be affected by pressure at 298 K? Express your answer in terms of $\Delta G_{rx}^{o} = f(P_f, P_s)$.

(b) (10 points) For the cases of $\rho_s/\rho_f = 3.0$ and $\rho_s = \rho_f$; describe how you could estimate the variation of P_f with T for the gypsum to anhydrite transformation. What other property information is required to make the estimate? In both cases ρ_f can be taken as 1000 kg/m^3.

> [Hint: consider using the reaction equilibrium constraint $\Sigma\, v_i\mu_i = 0$ directly to determine a relationship between P_f and T assuming that all phases remain pure.]

Solution:

At the reference state of $T = 298$ K and $P = 1$ bar:

$$\Delta G_{rx}^{o}(298\,\text{K}, 1\,\text{bar}) = -1321.7 + 2(-237.141) - (-1797.2)$$
$$\Delta G_{rx}^{o}(298\,\text{K}, 1\,\text{bar}) = 1.218\ \text{kJ/mol}$$

The problem asks us how ΔG^{o}_{rxn} will be affected by pressure. Since the reference state is defined as the temperature *and* pressure of the system, then ΔG^{o}_{rxn} will also vary with P. We want an expression for $\Delta G^{o}_{rxn}(298\ \text{K}, P)$. From Equation (16-45) in the textbook:

$$\left(\frac{\partial \Delta G^{o}_{rxn}}{\partial P}\right)_T = \sum_j \upsilon_j \left(\frac{\partial G^{o}_j}{\partial P}\right)_T$$
$$= \sum_j \upsilon_j \left(V^{o}_j\right)_T = \Delta V^{o}_{rxn}$$

However, the fluid phase and solid phases are at different pressures. Therefore, when integrating the above expression, the limits of integration will be different for the different phases:

$$\int_{1\text{ bar}}^{P_f,P_s} d\Delta G^o_{rxn} = \int_{1\text{ bar}}^{P_s} d\Delta V_{\text{gypsum}\to\text{anhydrite}} + 2\int_{1\text{ bar}}^{P_f} d\Delta V_{H_2O}$$

where P_f = pressure in the fluid phase and P_s = pressure in the solid phases. Assuming that the fluid and solid phases are incompressible:

$$\begin{aligned}\Delta G^o_{rxn}\left(298\text{ K}, P_f, P_s\right) &= \Delta G^o_{rxn}\left(298\text{ K, 1 bar}\right) + \Delta V_{\text{gypsum}\to\text{anhydrite}}\left(P_s - 1\right) + \Delta V_{H_2O}\left(P_f - 1\right)\\ &= 1.218\text{ kJ/mol} + \left(-29.48\ {}^{\text{cm}^3}\!/_{\text{mol}}\right)\left(P_s - 1\right) + 2\left(18.07\,{}^{\text{cm}^3}\!/_{\text{mol}}\right)\left(P_f - 1\right)\\ &= 1.217\text{ kJ/mol} + 2\left(18.07\,{}^{\text{cm}^3}\!/_{\text{mol}}\right)P_f - \left(29.48\ {}^{\text{cm}^3}\!/_{\text{mol}}\right)P_s\end{aligned}$$

Any of the above expressions is acceptable.

Some students tried to use the equation:

$$\Delta G^o_{rxn}\left(298\text{ K}, P_f, P_s\right) = -RT\ \ln K = -RT\ \ln \frac{\left({}^{f_a}\!/_{f_a^o}\right)\left({}^{f_{H_2O}}\!/_{f^o_{H_2O}}\right)^2}{\left({}^{f_g}\!/_{f_g^o}\right)}$$

and then looked for the variation in ΔG^o_{rxn} with P by calculating $(\partial \ln K/\partial P)_T$. Although this was a much more difficult route, the correct solution can be found via this method, and should match those shown from the method above. No student as able to complete the problem using this method though, due to its complexity.

(b)

Using the hint, and assuming that all phases are pure, then from a degree of freedom analysis:

$\mathcal{F} = 3 + 2 - 3 - 1 = 1$ d.o.f.

Therefore, since there is only one degree of freedom, once one variable (either T or P_f) is fixed, so are all the others. Note that P_f and P_s are related by their densities. Once the density of each phase is determined and either the depth (z) or one of the pressures is set, both pressures can be determined using the integrals that define the pressures above.

For pure components, $\mu_i = G_i$. Using the hint given to us in the problem statement:

$$0 = \sum_i \upsilon_i \mu_i = \sum_i \upsilon_i G_i$$

$$0 = G_{\text{anhydrite}}\left(T, P_s\right) + 2G_{H_2O}\left(T, P_f\right) - G_{\text{gypsum}}\left(T, P_s\right) = \Delta G^o_{rxn}\left(T, P_f, P_s\right)$$

Therefore, our restriction becomes that the $\Delta G^o_{rxn} = 0$. We already know how ΔG^o_{rxn} varies with pressure. Therefore, we must determine how it varies with temperature:

$$\left(\frac{\partial \Delta G^o_{rxn}}{\partial T}\right)_P = \sum_j \upsilon_j \left(\frac{\partial G^o_j}{\partial T}\right)_P$$

$$= \sum_j \upsilon_j \left(-S^o_j\right)_T = -\Delta S^o_{rxn}$$

We should note that ΔS^o_{rxn} has a slightly different definition from normal when $P_f \neq P_s$:

$$\Delta S^o_{rxn} = \Delta S^o_{\text{f, anhydrite}}\left(P_s\right) + \Delta S^o_{\text{f, H}_2\text{O}}\left(P_f\right) - \Delta S^o_{\text{f, gypsum}}\left(P_s\right)$$

Adding the variation of ΔG^o_{rxn} with respect to T to our solution from part (a), we have:

$$\Delta G^o_{rxn}\left(T, P_f, P_s\right) = \Delta G^o_{rxn}\left(298\text{ K, 1 bar}\right) + \Delta V_{\text{gypsum}\rightarrow\text{anhydrite}}\left(P_s - 1\right) + \Delta V_{H_2O}\left(P_f - 1\right) - \int_{298\text{ K}}^{T} \Delta S^o_{rxn} dT = 0$$

$$= 1.218\text{ kJ/mol} + \left(-29.48\ {\text{cm}^3}/{\text{mol}}\right)\left(P_s - 1\right) + 2\left(18.07\,{\text{cm}^3}/{\text{mol}}\right)\left(P_f - 1\right) - \int_{298\text{ K}}^{T} \Delta S^o_{rxn} dT = 0$$

$$= 1.217\text{ kJ/mol} + 2\left(18.07\,{\text{cm}^3}/{\text{mol}}\right)P_f - \left(29.48\ {\text{cm}^3}/{\text{mol}}\right)P_s - \int_{298\text{ K}}^{T} \Delta S^o_{rxn} dT = 0$$

It should be noted that for the first case, $P_f = P_s = P$, whereas for the second case: $P_s = 3P_f$.

Property information needed to do this problem are values for the densities of the phases and an expression for $\Delta S^o_{rxn} = \text{f}(T, P)$.

Another possible option would have been to use K:

$$\Delta G^o_{rxn}\left(298\text{ K}, P_f, P_s\right) = -RT\ \ln K = -RT\ \ln \frac{\left({f_a}/{f^o_a}\right)\left({f_{H_2O}}/{f^o_{H_2O}}\right)^2}{\left({f_g}/{f^o_g}\right)}$$

Note that the standard state is 298 K and the pressure of the system. This method would require knowledge of how the fugacities vary with temperature. Many students related $(\partial \ln f_i/\partial T)_P$ to $-H_i/T^2$, although few were able to do so successfully. In this case the enthalpy of reaction was required to reach a solution. Other students calculated $(dP/dT)_{\text{equil}}$ using methods in Chapter 17. This also resulted in the need for the enthalpy of reaction, but was also accepted if done correctly. However, the simplest method is still that shown above for part (b).