Geological Sciences 455: Geochemistry

PROBLEM SET ONE DUE SEPT. 12, 2007

1.) Show that

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$$

(hint: this is one of the Maxwell Relationships).

We begin with equation 2.120: dA = – SdT – PdV
we can also express dA as:

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \qquad (1)$$

so it is apparent that:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P \qquad (2)$$

Since A is a state function, then:

$$\left(\frac{\partial^2 A}{\partial T \partial V}\right) = \left(\frac{\partial^2 A}{\partial V \partial T}\right) \text{ and } \left(-\frac{\partial S}{\partial V}\right)_T = \left(-\frac{\partial P}{\partial T}\right)_V \qquad (3)$$

Now we want to show that $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$

We can express volume as a function of T and P as:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad (4)$$

From the definition of α and β,

$$dV = V\alpha dT - V\beta dP \qquad (5)$$

at constant volume dV = 0, so

$$V\alpha dT - V\beta dP = 0 \qquad (6)$$

With some rearranging: $\frac{dP}{dT} = \frac{\alpha}{\beta}$ (7)

We derived this under the condition of constant volume, so the term on the left is actually the constant volume derivative, i.e.:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta} \qquad (8)$$

Substituting (8) into (3), we have: $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$

2.) Complete the proof that V is a state variable by showing that for an ideal gas:

$$\frac{\partial \alpha V}{\partial P} = -\frac{\partial \beta V}{\partial T}$$

Our definition of α and β are: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

The ideal gas law states that: $V = \frac{RNT}{P}$

By differentiating this expression

with respect to T holding P constant, we find: $\left(\frac{\partial V}{\partial T}\right)_P = \frac{RN}{P}$ and hence $\alpha = \frac{RN}{PV}$

and with respect to P we obtain: $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RNT}{P^2}$ and hence $\beta = \frac{RNT}{P^2 V}$

Substituting these expressions for α and β into our original expression, we have:

$$\frac{\partial(\frac{RN}{P})}{\partial P} = -\frac{\partial(\frac{RNT}{P^2})}{\partial T}$$

and finally performing the differentiation on each side, we have:

$$-\frac{RN}{P^2} = -\frac{RN}{P^2}$$

3.) A quartz crystal has a volume of 7.5 ml at 298 K and 0.1 MPa. What is the volume of the crystal at 840K and 12.3 MPa if

a.) $\alpha = 1.4654 \times 10^{-5}$ K^{-1} and $\beta = 2.276 \times 10^{-11}$ Pa^{-1} and α and β are independent of T and P.

b.) $\alpha = 1.4310 \times 10^{-5}\ \mathrm{K}^{-1} + 1.1587 \times 10^{-9}\ \mathrm{K}^{-2}T - 1.1484 \times 10^{-14}\ \mathrm{K}^{-1}\mathrm{Pa}^{-1} P$

$\beta = 1.8553 \times 10^{-11}\mathrm{Pa}^{-1} + 1.1484 \times 10^{-14}\mathrm{K}^{-1}\mathrm{Pa}^{-1}T + 7.9453 \times 10^{-8}\ P^{-1}$

Our expression for volume change as a function of T and P is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad (4)$$

Substituting expressions for α and β:

$$dV = V\alpha dT - V\beta dP \qquad (5)$$

We need to integrate to the desired temperature and pressure. First, we arrange the equation to get the appropriate form:

$$\frac{1}{V}dV = \alpha dT - \beta dP \qquad (5)$$

Integrating: $\int_{7.5}^{V} \frac{1}{V} dV = \int_{298}^{840} \alpha dT - \int_{0.1}^{12.3} \beta dP$

For part a.) we obtain:

$$\ln\left(\frac{V}{V_0}\right) = \left[-\beta P \right]_{P=0.1}^{P=12.3} + \left[\alpha T \right]_{T=298}^{T=840}$$

Calculating the result, we find **V = 7.5577 ml.**

For part b.), our expression to integrate is:

$$\int_{7.5}^{V} \frac{1}{V} dV = \int_{298}^{840} (1.431\times10^{-5} + 1.1587\times10^{-9}T - 1.1484\times10^{-10}P)dT$$

$$-\int_{0.1}^{12.3} (1.8553\times10^{-11} + 1.15\times10^{-14}T + \frac{7.9453\times10^{-8}}{P})dP$$

We imagine that we first raise temperature, then pressure. So we do the first integration at 0.1 MPa over the temperature range, and the second integration at 840K over the pressure range. We can substitute these values into the expression and simplify it a bit:

$$\int_{7.5}^{V} \frac{1}{V} dV = \int_{298}^{840} (1.431\times10^{-5} + 1.1587\times10^{-9}T)dT$$

$$-\int_{0.1}^{12.3} (1.8553\times10^{-11} + \frac{7.9453\times10^{-8}}{P})dP$$

$$\ln\frac{V}{V_0} = \left[1.431\times10^{-5}T + \frac{1.1587\times10^{-9}}{2}T^2 \right]_{298}^{840}$$

$$-\left[1.8553\times10^{-11}P + 7.9453\times10^{-8}\ln P \right]_{0.1}^{12.3}$$

The result is 7.5594 ml, only very slightly different from (a).

4.) One mole of an ideal gas is allowed to expand against a piston at constant temperature of 0°C. The initial pressure is 1 MPa and the final pressure is 0.04 MPa. Assuming the reaction is reversible,

a. What is the work done by the gas during the expansion?

Work is: $dW = -PdV$

To calculate the work, we need to evaluate the relationship between pressure and volume. Since it is the volume change that is prescribed, let's recast the equation in terms of pressure change.

$$dV = -V\beta dP = -\frac{V}{P}dP$$

Substituting, we have: $dW = -P\left(-\frac{V}{P}\right)dP = VdP$

Now we need to eliminate V from the equation, so we note that for an ideal gas:

$$V = \frac{NRT}{P}$$

So finally
$$dW = \frac{NRT}{P} dP$$

$$W = \int_1^{0.04} \frac{NRT}{P} dP = RT \ln \frac{0.04}{1} = -7309 J$$

b. What is the change in the internal energy and enthalpy of the gas?

The internal energy change associated with a volume change is given by equation 2.61:

$dU = \left(\frac{T\alpha}{\beta} - P \right) dV$ substituting $\alpha = 1/T$, $\beta = 1/P$, and we have: $dU = (P - P)\ dV = 0$

i.e., **dU = 0**; there is no energy change associated with the volume change of an ideal gas.

The enthalpy change is defined by equ. 2.63 as:

$$dH = dU + VdP + PdV$$

Since dU = 0, and (for an ideal gas) V=NRT/P we may write this as:

$$dH = 0 + NRTdP/P + PdV$$

From the ideal gas law, we find that $dV = -NRT/P^2dP$ Substituting for dV in the above, we have:

$$dH = NRTdP/P - NRT/PdP = 0$$

We see that the enthalpy change associated with an isothermal process is 0 for an ideal gas.

c. How much heat is gained/lost during the expansion?

To answer this, we use the first law:

$\Delta U = \Delta Q + \Delta W$; since $\Delta U = 0$, $\mathbf{\Delta Q = -\Delta W = 7036\ J}$.

5.) Calcite and aragonite are two forms of $CaCO_3$ that differ only their crystal lattice structure. The reaction between them is thus simply:

$$\text{Calcite} \rightleftarrows \text{Aragonite}$$

Using the data in Table 2.2,

a.) Determine which of these forms is stable at the surface of the earth (25° C and 0.1 MPa).

The side of the reaction having the lowest Gibbs Free Energy is stable. According to Table 2.2,
G_{Cal} = -1130.10 and G_{Arag} = --1129.16, so calcite is stable.

b.) Which form is favored by increasing temperature?

If ΔG decreases with increasing temperature, then the product (left) side of the reaction will be favored and visa versa. The trick here is to note that $\left(\frac{\partial \Delta G_r}{\partial T}\right)_P = -\Delta S_r$, so if ΔS is positive, aragonite will be favored and visa versa. Using Hess's Law, we find ΔS_r = 90.21-92.68. ΔS will be negative, so calcite is favored by increasing T.

c.) Which form is favored by increasing pressure?

Similarly, we note that $\left(\frac{\partial \Delta G_r}{\partial P}\right)_T = \Delta V_r$. If ΔG decreases with increasing pressure, then the product (left) side of the reaction will be favored and visa versa. ΔV_r = 34.15-36.93. ΔV is negative, so aragonite is favored by increasing pressure.

6.) For a pure olivine mantle, calculate the adiabatic temperature gradient $(\partial T/\partial P)_S$ at 0.1 MPa (1 atm) and 1000°C. Use the thermodynamic data in Table 2.2 for forsterite (Mg-olivine, Mg_2SiO_4) and $\alpha = 44 \times 10^{-6}\ K^{-1}$, and $\beta = 8\times10^{-6}\ MPa^{-1}$.
Note that: 1 cc/mol = 1 J/MPa/mol.

We want to know how temperature varies with pressure under the condition of constant entropy. We can write the following expression:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = 0$$

Rearranging:

$$\left(\frac{\partial T}{\partial P}\right)_S = {-\left(\frac{\partial S}{\partial P}\right)_T} \Big/ {\left(\frac{\partial S}{\partial T}\right)_P}$$

Substituting from equations 2.105 and 2.147:

$$\left(\frac{\partial T}{\partial P}\right)_S = {\left(\frac{\partial V}{\partial T}\right)_T} \Big/ {\frac{C_P}{T}} = \frac{V\alpha T}{C_P}$$

Substituting values from Table 2.2:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{43.79 J/MPa-mol \times 44 \times 10^{-6} K^{-1} \times 1273K}{149.83 + 0.02736 \times 1273 - \frac{3564768}{1273^2} J/K-mol} = .0131 K/MPa$$