ESS 312: WEEK 3 - MAKING DIAMONDS

Kimberlite is an unusual rock type that is famous as a source of diamonds. The diamonds are transported to the surface during eruption of the kimberlite. This means that kimberlite forms deep enough in the mantle so that when it rises it passes through the stability field of diamond. If we can calculate the conditions for diamond stability we can draw some conclusions about how deep these eruptions started. In this problem set we will examine the reaction: **GRAPHITE ↔ DIAMOND**, and use thermodynamic data to investigate the stabilities of these C polymorphs as functions of pressure and temperature.

The following are some useful thermodynamic data from tables compiled by Robie and others (1978) published by the U.S. Geological Survey. *Pay attention to units. You will need to use the following conversion factor: 1 cm^3 = 0.10 J/bar*

	$S^o_{(298\ K,\ 1\ bar)}$ J/mol-K	$\Delta H^o_{f,\ (298K,\ 1\ bar)}$ kJ/mol
diamond	2.4	1.9
graphite	5.7	0.0
CO_2	213.7	-393.5
O_2	205.1	0.0

	$V_{(298K,\ 1\ bar)}$	*C_p
diamond	3.417 (cm^3/mol)	11.62 + 0.01 T (J/mol K)
graphite	5.299 (cm^3/mol)	15.6 + 0.006 T (J/mol K)

*These simplified heat capacity expressions are strictly only relevant to temperatures in the range 1000 K – 1800 K, but we will use them here for the range 298 K – 1300 K.

1. Because of the extreme pressures required to stabilize diamond, it is difficult to determine experimentally the ΔS and ΔH associated with the reaction **GRAPHITE ↔ DIAMOND**. However, we can extract these data from consideration of the following reactions:

$$\textbf{graphite} + O_2 \leftrightarrow CO_2$$

$$\textbf{diamond} + O_2 \leftrightarrow CO_2$$

(a) Calculate the changes in enthalpy and entropy associated with these two reactions at 298 K and 1 bar.

(b) Combine these reactions to obtain ΔH and ΔS for the reaction:

graphite ↔ diamond

(c) Use these data to calculate ΔG for the reaction at 298K, 1 bar and indicate which polymorph is stable under these conditions. Verify your answer using what you know about the relative stability of these two minerals.

2. Now consider this reaction at temperatures and pressures more realistic for the mantle.

(a) Write the general equation that describes the free energy change of a reaction at any temperature T and at the reference P_r of 1 bar (i.e., at T = any T and $P = P_r$).

(b) Use this equation and the results from 1) to calculate the free energy change of the graphite – diamond reaction at 1300K and 1 bar.

(c) Now add the necessary term to the equation in 2(a) so that you can calculate the free energy change for any reaction at any temperature and any pressure (i.e., at T and P).

(d) Use this equation to calculate the pressure required for diamond and graphite to coexist at equilibrium at 1300K. For this calculation *assume that the coefficients of thermal expansion and isothermal compressibility are both equal to zero*.

3. Use the Clapeyron equation to calculate the slope of the graphite-diamond equilibrium curve in P-T space. Plot this curve and predict which polymorph is stable at 3.5 GPa and 1100K.

4. Diamonds are erupted in explosive volcanic rocks called kimberlites. A group of kimberlites in South Africa has a characteristic mineralogy and type of diamond that sets it apart from other diamond occurrences. These kimberlites are only found on continental crust that is Archean in age. None of these types of kimberlites is found in adjoining but younger crust. Minerals in the kimberlite rock allow us to determine that the eruption occurred about 90 million years ago (Ma). There are also mineral inclusions *within* these diamonds that allow us to determine the age of the diamonds themselves. They did not form 90 Ma during eruption of the kimberlite, but formed 3.3 to 3.5 billion years ago (Ga). We also know that the kimberlitic magma formed at a temperature of 900° - 1300°C from a source that has a mineralogy similar to garnet-bearing mantle peridotite.

Using this information and what you calculated for diamond – graphite equilibrium, what do your results imply about the origin of these diamonds, and the structure and development of the oldest (Archean) continents preserved on Earth?