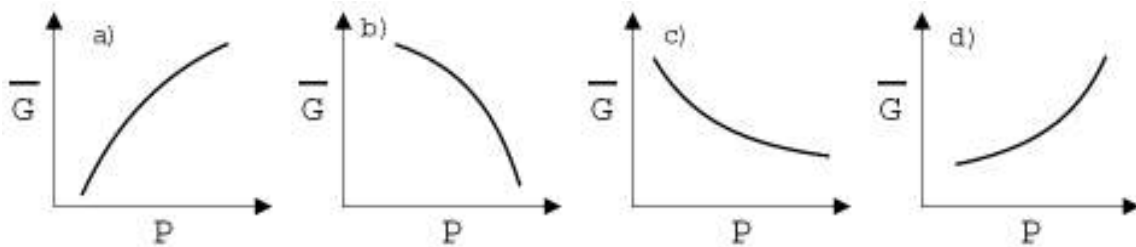


PHYS 324 – Thermodynamics
Spring 2008

Homework 7: (due March 6th)

1. Which of the following figures illustrates the correct dependence of the molar Gibbs free energy on the pressure at constant temperature for a solid? Explain your choice.



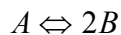
2. For the reaction $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$
- Write down a general expression for the partial pressure of oxygen, P_{O_2} , at equilibrium using the concept of the equilibrium constant and its relation to the free energy of reaction, $\Delta\bar{G}_{reaction}$.
 - For a fixed P_{CO_2} / P_{CO} ratio, make schematic plots that show the relation between P_{O_2} and P_{Total} as well as P_{O_2} and T . [Hint: the second plot will be easier to schematically draw if you plot $\ln(P_{O_2})$ as a function of $1/T$.]
 - For a general reaction beginning with $n_{CO}^{initial}$, $n_{O_2}^{initial}$ and $n_{CO_2}^{initial}$ moles of the substances write down an expression for the reaction constant in terms of the final number of moles (x) of O_2 .
3. For a system that can only do electric work derive the four Maxwell Relations from the different potentials and sketch the corresponding mnemonic diagram.
4. Determine whether the following statements are true or false. You will only receive full credit if you fully explain your reasoning.
- The total entropy of a system at constant volume and temperature is never observed to decrease spontaneously.
 - At global equilibrium, the Gibbs free energy of an isolated system attains its lowest possible value.

The next three rely on the following set-up: At one atmosphere pressure, a solution composed of Iron and Ruthenium can have three possible equilibrium crystal structures: FCC, BCC and HCP. Consider a reservoir with fixed P and T that is simultaneously in equilibrium with FCC, BCC and HCP solutions of Fe-Ru.

- (c) If the FCC and BCC solutions can freely exchange both iron and ruthenium atoms, then the system can not be in equilibrium.
 - (d) If the FCC and BCC solutions can freely exchange both iron and ruthenium atoms, then the composition of the two solutions must be the same at equilibrium.
 - (e) If the FCC and BCC solutions can freely exchange both iron and ruthenium atoms, then their Gibbs free energies must be equal at equilibrium.
5. A student makes the following statement: “A mole of pure carbon in a graphite crystalline lattice has about twice the entropy content as a mole in a pure carbon diamond cubic crystalline lattice. Therefore, pure carbon-graphite is more disordered than pure carbon-diamond.”

- (a) Provide a descriptive definition of entropy, using pictures if necessary.
- (b) Is the student’s statement *necessarily* true based solely on the information provided in the statement?

6. Consider the following arbitrary gaseous reaction:



For a system that has *only* the gases A and B present, it is determined that at $T=1430\text{ K}$ and $P_{\text{total}} = 1\text{ atm}$, the mole fractions of A and B are equal ($X_A=X_B$). Approximating the system as an ideal gas mixture, find the mole fraction of A at the same temperature ($T=1430\text{ K}$) but at a total pressure $P_{\text{total}} = 3/8\text{ atm}$.