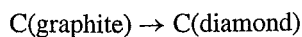


SOLUTIONS

PROBLEM SET 5

CHM 3400, Dr. Chatfield

4.34 This problem involves the synthesis of diamond from graphite:



(a) Calculate the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for the reaction. Will the conversion be favored at 25° C or any other temperature? (b) From density measurements, the molar volume of graphite is found to be 2.1 cm³ greater than that of diamond. Can the conversion of graphite to diamond be brought about at 25° C by applying pressure on graphite? If so, estimate the pressure at which the process becomes spontaneous. [Hint: Starting from Equation 4.32, derive the equation $\Delta_r G_2 - \Delta_r G_1 = (\bar{V}_{\text{diamond}} - \bar{V}_{\text{graphite}}) \Delta P$ for a constant-temperature process. Next, calculate the ΔP value that would lead to the necessary decrease in Gibbs energy.]

$$\begin{aligned} \text{(a)} \quad \Delta_r H^\circ &= \Delta_f \bar{H}^\circ [\text{C(diamond)}] - \Delta_f \bar{H}^\circ [\text{C(graphite)}], \\ &= 1.90 \text{ kJ mol}^{-1} - 0 \text{ kJ mol}^{-1} \\ &= 1.90 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ &= \bar{S}^\circ [\text{C(diamond)}] - \bar{S}^\circ [\text{C(graphite)}] \\ &= 2.4 \text{ J K}^{-1} \text{ mol}^{-1} - 5.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -3.3 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

At 25° C,

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - (298 \text{ K}) \Delta_r S^\circ \\ &= 1.90 \text{ kJ mol}^{-1} - (298 \text{ K}) (-3.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= 2.883 \text{ kJ mol}^{-1} = 2.88 \text{ kJ mol}^{-1} \end{aligned}$$

Therefore, the conversion from graphite to diamond is not spontaneous at 25° C and when both are in their standard states. In fact, because $\Delta_r H^\circ$ is positive and $T \Delta_r S^\circ$ is negative, $\Delta_r G^\circ$ can never be negative. Thus, the conversion will not be spontaneous at any other temperature.

(b) The integration of Equation 4.32

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

gives

$$G_2 = G_1 + V (P_2 - P_1)$$

where G_1 and G_2 are the Gibbs energies at P_1 and P_2 , respectively. Using molar quantities and $\Delta P = P_2 - P_1$, the equation becomes

$$\bar{G}_2 = \bar{G}_1 + \bar{V} \Delta P$$

Apply this equation to graphite and diamond,

$$\begin{aligned} \bar{G}_2 [\text{graphite}] &= \bar{G}_1 [\text{graphite}] + \bar{V} [\text{graphite}] \Delta P \\ \bar{G}_2 [\text{diamond}] &= \bar{G}_1 [\text{diamond}] + \bar{V} [\text{diamond}] \Delta P \end{aligned}$$

These two equations are combined to relate the values of $\Delta_r G$ for the conversion of graphite to diamond at two different pressures:

$$\begin{aligned}\Delta_r G_2 &= \bar{G}_2 [\text{diamond}] - \bar{G}_2 [\text{graphite}] \\ &= \left\{ \bar{G}_1 [\text{diamond}] + \bar{V} [\text{diamond}] \Delta P \right\} - \left\{ \bar{G}_1 [\text{graphite}] + \bar{V} [\text{graphite}] \Delta P \right\} \\ &= \Delta_r G_1 + \left\{ \bar{V} [\text{diamond}] - \bar{V} [\text{graphite}] \right\} \Delta P\end{aligned}$$

If $P_1 = 1$ bar, then $\Delta_r G_1 = \Delta_r G^\circ = 2.883 \text{ kJ mol}^{-1}$ at 25°C . $\Delta_r G_2$ becomes

$$\begin{aligned}\Delta_r G_2 &= 2.883 \text{ kJ mol}^{-1} + (-2.1 \text{ cm}^3 \text{ mol}^{-1}) \Delta P \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) \left(\frac{1 \text{ atm}}{1.013 \text{ bar}} \right) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= 2.883 \text{ kJ mol}^{-1} - 2.1 \times 10^{-4} \Delta P \text{ kJ bar}^{-1} \text{ mol}^{-1}\end{aligned}$$

If the process is spontaneous, then

$$\begin{aligned}\Delta_r G_2 &= 2.883 \text{ kJ mol}^{-1} - 2.1 \times 10^{-4} \Delta P \text{ kJ bar}^{-1} \text{ mol}^{-1} < 0 \\ 2.883 \text{ kJ mol}^{-1} &< 2.1 \times 10^{-4} \Delta P \text{ kJ bar}^{-1} \text{ mol}^{-1} \\ \Delta P &> \frac{2.883 \text{ kJ mol}^{-1}}{2.1 \times 10^{-4} \text{ kJ bar}^{-1} \text{ mol}^{-1}} = 1.4 \times 10^4 \text{ bar}\end{aligned}$$

Therefore, at a very high pressure, $P_2 = \Delta P + P_1 = 1.4 \times 10^4 \text{ bar} + 1 \text{ bar} = 1.4 \times 10^4 \text{ bar}$, the conversion from graphite to diamond is spontaneous.

4.36 Predict the signs of ΔH , ΔS , and ΔG of the system for the following processes at 1 atm: (a) ammonia melts at -60°C , (b) ammonia melts at -77.7°C , and (c) ammonia melts at -100°C . (The normal melting point of ammonia is -77.7°C .)

Since melting is an endothermic process, ΔH is positive in all three cases. A substance in the liquid phase is more disordered than in the solid phase. Therefore, ΔS is positive in all three cases.

When the temperature is above the melting point, the melting process is spontaneous, that is, ΔG is negative. When the temperature is at the melting point, the melting process is at equilibrium, that is, ΔG is zero. When the temperature is below the melting point, the melting process is not spontaneous, that is, ΔG is positive.

In summary,

(a) ΔH : +, ΔS : +, ΔG : -

(b) ΔH : +, ΔS : +, ΔG : 0

(c) ΔH : +, ΔS : +, ΔG : +

- 4.42 The pressure exerted on ice by a 60.0-kg skater is about 300 atm. Calculate the depression in freezing point. The molar volumes are $\bar{V}_L = 0.0180 \text{ L mol}^{-1}$ and $\bar{V}_S = 0.0196 \text{ L mol}^{-1}$.

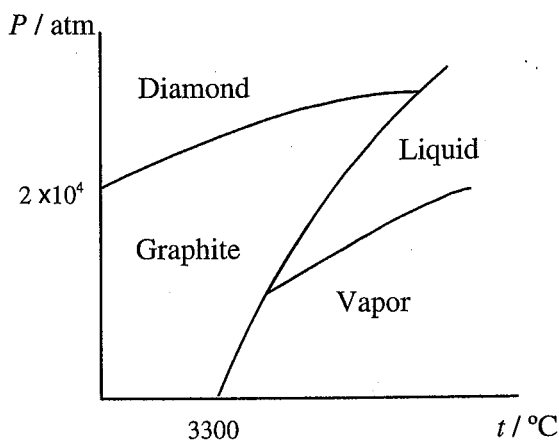
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The depression of freezing point can be obtained from the slope of the S-L curve in the phase diagram.

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta\bar{H}}{T\Delta\bar{V}} = \frac{(6.01 \times 10^3 \text{ J mol}^{-1}) \left(\frac{1 \text{ L atm}}{101.3 \text{ J}}\right)}{(273.2 \text{ K}) (0.0180 \text{ L mol}^{-1} - 0.0196 \text{ L mol}^{-1})} \\ &= -135.7 \text{ atm K}^{-1} \\ dP &= -135.7 \text{ atm K}^{-1} dT \\ \int_{1 \text{ atm}}^{300 \text{ atm}} dP &= -135.7 \text{ atm K}^{-1} \int_{273.15 \text{ K}}^{T \text{ K}} dT \\ 299 \text{ atm} &= -135.7 \text{ atm K}^{-1} \Delta T \\ \Delta T &= \frac{299 \text{ atm}}{-135.7 \text{ atm K}^{-1}} = -2.20 \text{ K} \end{aligned}$$

Therefore, the freezing point is depressed by 2.20 K when 300 atm is applied to ice. In other words, the freezing point at this pressure is $273.15 \text{ K} - 2.20 \text{ K} = 270.95 \text{ K}$ or -2.20°C .

- 4.46 Below is a rough sketch of the phase diagram of carbon. (a) How many triple points are there, and what are the phases that can coexist at each triple point? (b) Which has a higher density, graphite or diamond? (c) Synthetic diamond can be made from graphite. Using the phase diagram, how would you go about making diamond?



- (a) There are two triple points. At one triple point, diamond, graphite and liquid carbon coexist. At the other, graphite, liquid carbon, and gaseous carbon coexist.

(b) According to the Clapeyron equation, $\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$. From the phase diagram, the graphite-diamond curve has positive slope for most of its length. From Problem 4.34, the standard molar enthalpy change for $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$, $\Delta\bar{H}^\circ$, is also positive. This implies that $\Delta\bar{V}$ is positive, or that diamond has a greater molar volume than graphite. Consequently, one would conclude that diamond is less dense than graphite. In fact this conclusion is in error, and diamond is the denser phase. The problem is that by using $\Delta\bar{H}^\circ$, the assumption is made that ΔH is independent of pressure. Indeed, the evidence suggests that it changes sign and is negative at those pressures where graphite and diamond are in equilibrium.

- (c) The phase diagram indicates that high pressures are required to convert graphite to diamond.

- 4.50 The normal boiling point of ethanol is 78.3° C, and its molar enthalpy of vaporization is 39.3 kJ mol⁻¹. What is its vapor pressure at 30° C?

$$\ln \frac{P_2}{P_1} = -\frac{\Delta_{\text{vap}}\overline{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_2}{1 \text{ atm}} = -\frac{39.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{303.2 \text{ K}} - \frac{1}{351.5 \text{ K}} \right) = -2.142$$

$$P_2 = (1 \text{ atm}) e^{-2.142} = 0.117 \text{ atm} = 88.9 \text{ torr}$$

- 4.51 Entropy has sometimes been described as “times’s arrow” because it is the property that determines the forward direction of time. Explain.

Because the second law of thermodynamics requires that the entropy of the universe is always increasing, then it would be possible to order two points in time by determining the entropy of the universe at those times. The time corresponding to the greater entropy in the universe is the later time.

- 4.56 One mole of an ideal monatomic gas is compressed from 2.0 atm to 6.0 atm while being cooled from 400 K to 300 K. Calculate the values of ΔU , ΔH , and ΔS for the process.

The thermodynamic quantities can be readily calculated by breaking down the process into 2 steps: (1) isothermal compression at 400 K from 2.0 atm to 6.0 atm; (2) cooling at constant pressure (6.0 atm) from 400 K to 300 K.

Step 1

For an ideal gas undergoing an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2} = (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{2.0 \text{ atm}}{6.0 \text{ atm}} = -9.13 \text{ J K}^{-1}$$

Step 2

$$\Delta H = C_P \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (300 \text{ K} - 400 \text{ K}) = -2.079 \times 10^3 \text{ J}$$

$$\Delta U = \Delta H - nR \Delta T = -2.079 \times 10^3 \text{ J} - (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (300 \text{ K} - 400 \text{ K})$$

$$= -1.248 \times 10^3 \text{ J}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} = \frac{5}{2} nR \ln \frac{T_2}{T_1} = \frac{5}{2} (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{300 \text{ K}}{400 \text{ K}} = -5.979 \text{ J K}^{-1}$$

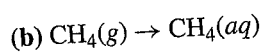
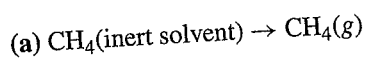
For the entire process,

$$\Delta H = 0 \text{ J} - 2.079 \times 10^3 \text{ J} = -2.08 \times 10^3 \text{ J}$$

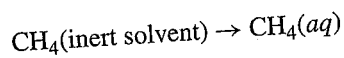
$$\Delta U = 0 \text{ J} - 1.248 \times 10^3 \text{ J} = -1.25 \times 10^3 \text{ J}$$

$$\Delta S = -9.13 \text{ J K}^{-1} - 5.979 \text{ J K}^{-1} = -15.1 \text{ J K}^{-1}$$

4.66 Protein molecules are polypeptide chains made up of amino acids. In their physiologically functioning or native state, these chains fold in a unique manner such that the nonpolar groups of the amino acids are usually buried in the interior region of the proteins, where there is little or no contact with water. When a protein denatures, the chain unfolds so that these nonpolar groups are exposed to water. A useful estimate of the changes of the thermodynamic quantities as a result of denaturation is to consider the transfer of a hydrocarbon such as methane (a nonpolar substance) from an inert solvent (such as benzene or carbon tetrachloride) to the aqueous environment:



If the values of ΔH° and ΔG° are approximately 2.0 kJ mol^{-1} and $-14.5 \text{ kJ mol}^{-1}$, respectively, for (a) and $-13.5 \text{ kJ mol}^{-1}$ and 26.5 kJ mol^{-1} , respectively, for (b), calculate the values of ΔH° and ΔG° for the transfer of 1 mole of CH_4 according to the equation



Comment on your results. Assume $T = 298 \text{ K}$.

For the process $\text{CH}_4(\text{inert solvent}) \rightarrow \text{CH}_4(aq)$

$$\Delta H^\circ = 2.0 \text{ kJ mol}^{-1} - 13.5 \text{ kJ mol}^{-1} = -11.5 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -14.5 \text{ kJ mol}^{-1} + 26.5 \text{ kJ mol}^{-1} = 12.0 \text{ kJ mol}^{-1}$$

Since $\Delta G^\circ > 0$, the process is not spontaneous when the reactant and product are in their standard states. Furthermore,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-11.5 \text{ kJ mol}^{-1} - 12.0 \text{ kJ mol}^{-1}}{298 \text{ K}} \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = -78.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

This negative value of ΔS° indicates that there is a decrease in order when CH_4 is dissolved in H_2O . This is a result of order imposed on the solvent (water) molecules, due to the special arrangement of water molecules around each CH_4 molecule (see Section 13.6).

5.10 Calculate the changes in entropy for the following processes: **(a)** mixing of 1 mole of nitrogen and 1 mole of oxygen, and **(b)** mixing of 2 moles of argon, 1 mole of helium, and 3 moles of hydrogen. Both **(a)** and **(b)** are carried out under conditions of constant temperature (298 K) and constant pressure. Assume ideal behavior.

$$\begin{aligned} \text{(a)} \quad \Delta_{\text{mix}}S &= -nR (x_{\text{N}_2} \ln x_{\text{N}_2} + x_{\text{O}_2} \ln x_{\text{O}_2}) \\ &= - (2 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = 11.53 \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta_{\text{mix}}S &= -nR (x_{\text{Ar}} \ln x_{\text{Ar}} + x_{\text{He}} \ln x_{\text{He}} + x_{\text{H}_2} \ln x_{\text{H}_2}) \\ &= - (6 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \left(\frac{2}{6} \ln \frac{2}{6} + \frac{1}{6} \ln \frac{1}{6} + \frac{3}{6} \ln \frac{3}{6} \right) = 50.45 \text{ J K}^{-1} \end{aligned}$$

5.12 Which of the following has a higher chemical potential? If neither, answer "same." **(a)** $\text{H}_2\text{O}(s)$ or $\text{H}_2\text{O}(l)$ at water's normal melting point, **(b)** $\text{H}_2\text{O}(s)$ at -5°C and 1 bar or $\text{H}_2\text{O}(l)$ at -5°C and 1 bar, **(c)** benzene at 25°C and 1 bar or benzene in a 0.1 M toluene solution in benzene at 25°C and 1 bar.

The less stable species of a pair has a higher chemical potential. When both substances in a pair are at equilibrium, then they have the same chemical potential.

(a) Same

(b) $\text{H}_2\text{O}(l)$ at -5°C and 1 bar

(c) Benzene at 25°C and 1 bar. This is because $x_{\text{benzene}} < 1$ in the following relation:

$$\mu_{\text{benzene}}(l) = \mu_{\text{benzene}}^*(l) + RT \ln x_{\text{benzene}}$$

Therefore,

$$\mu_{\text{benzene}}(l) < \mu_{\text{benzene}}^*(l)$$