

**Name:**

**Chem 3321 test #1 practice solutions**

I want complete, detailed answers to the questions. Show all your work to get full credit.

**Problem 1**

At atmospheric pressure, liquid water and ice exist in equilibrium at 0 °C. At this temperature,  $\Delta H_{\text{fusion}} = 6.00 \text{ kJ/mol}$ . (Fusion is the phase transition from solid to liquid.) Also at this temperature, the heat capacity of ice is  $38.0 \text{ J K}^{-1} \text{ mol}^{-1}$  and the heat capacity of water is  $76.0 \text{ J K}^{-1} \text{ mol}^{-1}$ .

a) Calculate the molar entropy of fusion of H<sub>2</sub>O at 0 °C.

Solution:

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} = \frac{6}{273} = 22 \text{ J K}^{-1} \text{ mol}^{-1} \quad (1)$$

b) At -10 °C, calculate the molar entropy of freezing (opposite of fusion) of H<sub>2</sub>O. In other words, calculate the molar entropy change when supercooled water undergoes a phase transition to ice. Assume that the heat capacities of each phase are constant in the -10 °C to 0 °C temperature range.

Solution:

It helps to sketch out the thermodynamic cycle that is being used here. We have

$$\Delta S = \int_{263}^{273} C_P^{\text{liquid}} \frac{dT}{T} - 22 + \int_{273}^{263} C_P^{\text{solid}} \frac{dT}{T} \quad (2)$$

$$= (C_P^{\text{liquid}} - C_P^{\text{solid}}) \ln(273/263) - 22 = 1.42 - 22 = -20.6 \text{ J K}^{-1} \text{ mol}^{-1} \quad (3)$$

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6. Assume an insulated container is divided into half where one mole of neon is on one side of a partition and one mole of helium is on the other side. Both sides of the container are at 1 atm and 273 K. At some point the partition is removed and the gases mix. Assuming no heat is exchanged with the surroundings, find  $\Delta S_{Ne}$ ,  $\Delta S_{He}$  and the total entropy change for the system and the surroundings. (b) Comment from your result whether the process is spontaneous or not.

$$\textcircled{10} \quad \frac{\Delta \bar{S}_{mix}}{R} = -x_{Ne} \ln x_{Ne} - x_{He} \ln x_{He}$$

where  $x = \text{mole fraction} = 1/2$  for each one.

$$\Rightarrow \frac{\Delta \bar{S}_{mix}}{R} = \ln 2 = 0.693$$

Multiplying by  $R$  and by 2 moles, we get

$$\textcircled{5} \quad \Delta S_{mix} = 2\Delta S_{Ne} = 2\Delta S_{He} = 11.52 \text{ JK}^{-1}$$

$$\textcircled{5} \quad q_s = 0 \Rightarrow \Delta S_{surr} = 0$$

$$\Delta S_{TOT} = 11.52 \text{ JK}^{-1} \Rightarrow \text{Spontaneous.}$$

### **Problem 3**

One mole of a monoatomic ideal gas initially at  $T = 400$  K and  $V = 30.0$  L has its pressure doubled through an isothermal process in which  $w = 3.00$  kJ of work is performed on the gas.

a) Calculate  $\Delta S = \Delta S_{\text{system}}$ .

Solution: This is an isothermal process. There are two approaches (that give the same answer)

(i)

$$S = (3/2)R \ln T + R \ln V \Rightarrow \Delta S = R \ln(15/30) = -R \ln 2 = -5.76 \text{ JK}^{-1} \quad (6)$$

(ii) choose an isothermal reversible path:

$$q_{\text{rev}} = -w = nRT \int_{V_i}^{V_f} \frac{dV}{V} \quad (7)$$

Then  $\Delta S = q_{\text{rev}}/T$

b) Calculate  $\Delta S_{\text{surroundings}}$ .

isothermal so  $q + w = 0$ , thus

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T} = \frac{3 \text{ kJ}}{400 \text{ K}} = 7.5 \text{ JK}^{-1} \quad (8)$$

c) Is this process spontaneous or non-spontaneous? Support your answer with an explanation and/or calculations.

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{universe}} > 0 \quad (9)$$

Therefore spontaneous since the universe is isolated.

(Note: if you have read Chapter 22,  $\Delta G$  is not useful here because the pressure is changing.)

#### Problem 4

1.50 mol of an ideal gas at 450 K is expanded from an initial pressure of 5.00 bar to a final pressure of 1.00 bar.  $\bar{C}_P = 5/2 R$ . The expansion is isothermal and reversible. Calculate  $q$  and  $w$ .

Solution:

Isothermal, Reversible

$$\Delta U = \delta w + \delta q$$

$$\Delta U = 0 \longrightarrow \therefore \delta w = -\delta q$$

$$-q = w = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

Under constant T,

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$-q = w = -nRT \ln \left( \frac{P_1}{P_2} \right)$$

$$-q = w = -1.5 \text{ mol} \times 8.3145 \text{ Jmol}^{-1}\text{K}^{-1} \times 450 \text{ K} \times \ln \left( \frac{5.00 \text{ bar}}{1.00 \text{ bar}} \right)$$

$$-q = w = -9.03 \text{ kJ}$$