## **Chapter 3 Homework Questions**

- 3.1 Calculate  $\Delta S$  (for the system) when the state of 3. moles of a perfect gas at 25 °C and 1. atm is changed to 125 °C and 5. atm. Note: The constant pressure molar heat capacity of this gas is  $C_{p,m} = (5/2)R$ ,
- **3.2** A sample consisting of 3. moles of a diatomic perfect gas at -73 °C is compressed reversibly and adiabically until the temperature reaches -23. °C. For this gas,  $C_{V,m} = 27.5 \text{ J/mol} \cdot \text{K}$ . Calculate q, w,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for this process.
- 3.3 Calculate the changes in entropy of the system and the surroundings when a 14. g sample of N<sub>2</sub>(g) [M=28] at 1. bar and 25 °C doubles its volume in
  (a) a reversible isothermal expansion
  - (b) an irreversible isothermal expansion against  $p_{ex} = 0$ .
  - (c) a reversible adiabatic expansion
- **3.4** The enthalpy of vaporization of chloroform (CHCl<sub>3</sub>, M=119.4) is 29.4 kJ/mol at its normal boiling point of 62 °C. For the vaporization of 240. grams of CHCl<sub>3</sub> at its normal boiling point, calculate (a)  $\Delta$ S of the system and (b)  $\Delta$ S of the surroundings.
- **3.5** The normal boiling point of ethanol,  $C_2H_5OH$  [M=46], is 78 °C. The Enthalpy of Vaporization of ethanol is 38.6 kJ/mol.

Calculate q, w,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  when 150 grams of ethanol vapor is condensed to the liquid at 78 °C and 1 bar pressure.

**3.6** The normal melting point of ethanol,  $C_2H_5OH$  [M=46], is -114 °C. The Enthalpy of Fusion of ethanol is 9.45 kJ/mol.

Calculate q, w,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  when 150 grams of ethanol liquid crystallizes to the solid at -114 °C and 1 bar pressure.

**3.7** The normal boiling point of benzene is 80 °C = 353 K. The enthalpy of vaporization of benzene at its normal boiling point is  $\Delta_{vap}H = 35.7$  kJ/mol. The constant pressure molar heat capacities of the liquid and vapor are:  $C_{p,m}(l) = 138.7$  J/mol-K and  $C_{p,m}(g) = 35.1$  J/mol-K

Consider the vaporization of one mole of superheated benzene at 100 oC. Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$ , and  $\Delta S_{univ}$  for this process.

**3.8** The standard molar entropy of NH<sub>3</sub>(g) is 192.45 J/mol•K at 25 °C. The constant pressure heat capacity is temperature dependent and is given by:

$$C_{p,m} = a + bT + \frac{c}{T^2}$$
  $a = 29.8$  ,  $b = 2.5 \times 10^{-2}$  ,  $c = -1.6 \times 10^5$   
Calculate the entropy of 3. moles of NH<sub>3</sub>(g) at:  
(a) 100 °C  
(b) 500 °C

**3.9** The constant pressure heat capacity of  $F_2(g)$  is temperature dependent and given by:

$$C_{p,m} = a - \frac{b}{T}$$
 a = 39.6 J/mol-K and b = 2.5x10<sup>3</sup> J/mol

Consider 100 grams of  $F_2(g)$  [M = 38.] initially at a pressure of 2. bar and temperature of 600 °C. Calculate q, w,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$  for each of the following processes.

- (a) The gas is cooled to 300 °C at constant pressure.
- (b) The gas is cooled to 300 °C at constant volume
- **3.10** Use the standard molar entropies (at 298 K) in the table below to calculate the reaction entropies,  $\Delta_r S^{\circ}$ , for the following reactions.
  - (a)  $2 \text{ CH}_3\text{CHO}(g) + O_2(g) \rightarrow 2 \text{ CH}_3\text{COOH}(l)$ (b)  $\text{Hg}(l) + \text{Cl}_2(g) \rightarrow \text{HgCl}_2(s).$

## Compound Sm<sup>o</sup>

250.3 J/mol•K
205.1
159.8
76.0
223.1
146.0

**3.11** Use the standard Gibbs Energies of Formation (at 298 K) in the table below to calculate the reaction entropies,  $\Delta_r S^\circ$ , for the following reactions.

(a)  $2 \text{ CH}_3\text{CHO}(g) + O_2(g) \rightarrow 2 \text{ CH}_3\text{COOH}(l)$ (b)  $H_2(l) + Cl_2(g) \rightarrow H_2Cl_2(g)$ 

(b)  $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$ .

## Compound $\Delta_f G_m^o$

 $\begin{array}{ll} CH_{3}CHO(g) & -128.9 \ kJ/mol \\ CH_{3}COOH(l) & -389.9 \\ HgCl_{2}(s) & -178.6 \end{array}$ 

3.12 Use the standard molar entropies and the enthalpies of formation in the table below to calculate the standard Gibbs energy change (at 298 K) for the reaction:  $4 \text{ HCl}(g) + O_2(g) \rightarrow \text{Cl}_2(g) + 2 \text{ H}_2O(l)$ 

Compound	Smo	$\Delta_{\rm f} H_{\rm m}^{\rm o}$
HCl(g)	186.9 J/mol•K	-92.3 kJ/mol
$O_2(g)$	205.1	
Cl <sub>2</sub> (g)	69.9	
$H_2O(l)$	223.1	-285.8

- **3.13** Consider 70. grams of  $N_2(g)$  [M=28] initially at 40 °C and 25 L. The gas is compressed isothermally to a final volume of 500 mL. Calculate  $\Delta G$  for this process.
- 3.14 The change in the Gibbs Energy for a certain constant pressure process is given by:  $\Delta G = a + bT^2$ , a = +5620 J,  $b = 8.0 \times 10^{-2} \text{ J/K}^2$ . Calculate  $\Delta S$  for this process at 30 °C (in J/K)
- **3.15** Calculate the change in Gibbs Energy (in J) of 20. moles of liquid benzene  $(C_6H_6, M = 78 \text{ g/mol}, d = 0.88 \text{ g/mL})$  when the pressure on the sample is increased from 1.0 atm to 100 atm.
- **3.16** Calculate the change in Gibbs Energy (in J) of 20. moles of  $H_2(g)$  when the pressure on the sample is increased from 1.0 atm to 100 atm at 25 °C.
- A solid has two crystalline forms, A(s) and B(s). For the transition A(s) → B(s), ΔG°= +6.0 kJ/mol (i.e. at 1 bar pressure). The difference in molar volumes of the two forms is Vm(B) Vm(A) = ΔVm = -15 mL/mol. Calculate the pressure, in bar, at which the two forms will be in equilibrium.