University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2010

Homework Assignment #3. Problems are due Monday day 11 July.

1) Suppose 1 mole of water is initially at T=253K and P=1atm. The temperature is raised to T=400K by placing it in contact with hot iron pan that is maintained at T=400K. The pressure is maintained at P=1atm. Assume the heat capacity at constant pressure of ice C_P is constant between 253K and T=273K and equals 37 J K^{-1} mol^{-1}. Assume the heat capacity C_P of liquid water is constant and is equal to 75.3 J $K^{-1}mol^{-1}$. Assume finally that C_P of water vapor in the temperature range given is 33 JK^{-1} mol^{-1}. For water ΔH_{melt}=6010$Jmol^{-1}$ and ΔH_{vap}=40100 $Jmol^{-}$ Calculate ΔS_{sys} ,ΔS_{surr} , and $\Delta S_{universe}$

Solution:

It is safe to assume the water is ice at T=253K . It is not supercooled. Ice at T=253K contacting a pan maintained at T=400K has the following entropy changes:

$$\Delta S_{sys} = \Delta S_{water} = \int_{253}^{273} \frac{C_P^{ice}}{T} dT + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{273}^{373} \frac{C_P^{liq}}{T} dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{373}^{400} \frac{C_P^{vap}}{T} dT$$

$$= C_P^{ice} \ln\left(\frac{273}{253}\right) + \frac{\Delta H_{fusion}}{273K} + C_P^{liq} \ln\left(\frac{373}{273}\right) + \frac{\Delta H_{vap}}{373K} + C_P^{vap} \ln\left(\frac{400}{373}\right)$$

$$= \left(37JK^{-1}\right)\left(0.076\right) + \frac{6010J}{273K} + \left(75.3JK^{-1}\right)\left(0.312\right) + \frac{40100J}{373K} + \left(33JK^{-1}\right)\left(0.070\right)$$

$$= 2.81JK^{-1} + 22.01JK^{-1} + 23.49JK^{-1} + 107.5JK^{-1} + 2.31JK^{-1} = 158JK^{-1}$$

The entropy change for the surrounds is: $\Delta S_{surr} = \frac{\Delta H_{surr}}{T_{surr}} = -\frac{\Delta H_{sys}}{T_{surr}}$ …so we need to calculate the enthalpy change of the system.

$$\Delta H_{sys} = \Delta H_{water} = \int_{253}^{273} C_P^{ice} dT + \Delta H_{fusion} + \int_{273}^{373} C_P^{liq} dT + \Delta H_{vap} + \int_{373}^{400} C_P^{vap} dT$$

$$= C_P^{ice}\left(273K - 253K\right) + \Delta H_{fusion} + C_P^{liq}\left(373K - 273K\right) + \Delta H_{vap} + C_P^{vap}\left(400K - 373K\right)$$

$$= \left(37JK^{-1}\right)\left(20K\right) + 6010J + \left(75.3JK^{-1}\right)\left(100K\right) + 40100J + \left(33JK^{-1}\right)\left(27K\right)$$

$$= 740J + 6010J + 7530J + 40100J + 891J = 55271J$$

Now $\Delta S_{surr} = -\frac{\Delta H_{sys}}{T_{surr}} = -\frac{55271J}{400K} = -138JK^{-1}$

Entropy of the universe: $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} = 158JK^{-1} - 138JK^{-1} = 20JK^{-1}$

2) One mole of an ideal monatomic gas undergoes the following transformation from an initial state P=1 bar and T=300K. Calculate q, w, ΔU, ΔH, and ΔS for each process.

   a) The gas is heated to T=450K at a constant pressure of P=1.00 bar.

$$V_i = \frac{nRT_i}{P_i} = \frac{1\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K}}{10^5\text{Pa}} = 2.49 \times 10^{-2}\text{m}^3$$

$$V_f = \frac{T_f}{T_i} V_i = \frac{450\ \text{K}}{300\ \text{K}} \times 2.49 \times 10^{-2}\text{m}^3 = 3.74 \times 10^{-2}\text{m}^3$$

$$w = -P_{external}\Delta V = -10^5\text{Pa} \times \left(3.74 \times 10^{-2}\text{m}^3 - 2.49 \times 10^{-2}\text{m}^3\right) = -1.25 \times 10^3\ \text{J}$$

$$\Delta U = nC_{V,m}\Delta T = 1\ \text{mol} \times \frac{3 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2} \times 150\ \text{K} = 1.87 \times 10^3\text{J}$$

$$q = \Delta H = \Delta U - w = 1.87 \times 10^3\text{J} + 1.25 \times 10^3\text{J} = 3.12 \times 10^3\text{J}$$

$$\Delta S = nC_{P,m} \ln \frac{T_f}{T_i} = 1\ \text{mol} \times \left(\frac{3}{2} + 1\right) \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times \ln \frac{450\ \text{K}}{300\ \text{K}} = 8.43\ \text{J K}^{-1}$$

   b) The gas is heated to T=450K at constant volume.

$$w = 0 \text{ because } \Delta V = 0.$$

$$\Delta U = q = nC_{V,m}\Delta T = 1\ \text{mol} \times \frac{3 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2} \times 150\ \text{K} = 1.87 \times 10^3\text{J}$$

$$\Delta H = nC_{P,m}\Delta T = 1\ \text{mol} \times \frac{5 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2} \times 150\ \text{K} = 3.12 \times 10^3\text{J}$$

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} = 1\ \text{mol} \times \left(\frac{3}{2}\right) \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times \ln \frac{450\ \text{K}}{300\ \text{K}} = 5.06\ \text{J K}^{-1}$$

   c) The gas undergoes a reversible isothermal expansion at T=300K unitl its pressure is P=0.5 bar.

$$\Delta U = \Delta H = 0 \text{ because } \Delta T = 0.$$

$$w_{reversible} = -q = -nRT \ln \frac{V_f}{V_i} = -1\ \text{mol} \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K} \times \ln 2 = -1.73 \times 10^3\text{J}$$

$$\Delta S = \frac{q_{reversible}}{T} = \frac{1.73 \times 10^3\text{J}}{300\ \text{K}} = 5.76\ \text{J K}^{-1}$$

3) Calculate the entropy change if 2 moles of liquid ammonia at P= 1atm and T=233.2K are heated to T= 473K. The normal boiling point of ammonia is 239.7K. The heat of vaporization of ammonia is $\Delta H_{vap} = 23.2\text{kJmol}^{-1}$. The heat capacity of liquid ammonia is $C_P = 74.8\text{JK}^{-1}\text{mol}^{-1}$ and is constant from 233K to 239.7K. the heat capacity of ammonia gas between 239.7k and 473K is given by: $C_P = 33.6 + 29.3\times10^{-4}\left(\tfrac{T}{K}\right) + 21.3\times10^{-5}\left(\tfrac{T}{K}\right)^2 \text{ JK}^{-1}\text{mol}^{-1}$.

$$\Delta S = \int_{233.2K}^{239.7K} \frac{C_P^{(\ell)}}{T}dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{239.7K}^{473K} \frac{C_P^{(v)}}{T}dT$$

$$= \int_{233.2K}^{239.7K} \frac{74.8JK^{-1}mol^{-1}}{T}dT + \frac{23200Jmol^{-1}}{239.7K}$$

$$+ \int_{239.7K}^{473K} \left(33.6\left(\frac{T}{K}\right)^{-1} + 29.3\times10^{-4} + 21.3\times10^{-5}\left(\frac{T}{K}\right)\right) JK^{-1}mol^{-1}dT$$

$$= \left(74.8JK^{-1}mol^{-1}\right)\ln\left(\frac{239.7}{233.2}\right) + 96.8JK^{-1}mol^{-1} + 33.6JK^{-1}mol^{-1}\times\ln\left(\frac{473}{239.7}\right)$$

$$+29.3\times10^{-4}\,JK^{-1}mol^{-1}\times\left(473-239.7\right) + 21.3\times10^{-5}\,JK^{-1}mol^{-1}\left(\frac{473^2-239.7^2}{2}\right)$$

$$= 2.06JK^{-1}mol^{-1} + 96.8JK^{-1}mol^{-1} + 22.8JK^{-1}mol^{-1} + 0.68JK^{-1}mol^{-1} + 17.7JK^{-1}mol^{-1}$$

$$= 140JK^{-1}mol^{-1}$$

$$\therefore \Delta S = \left(2mol\right)\left(140JK^{-1}mol^{-1}\right) = 280JK^{-1}$$

4) Five moles of an ideal monatomic gas contract adiabatically and *irreversibly* when subjected to a constant external pressure of 1 atm from an initial volume V_1=200L and initial pressure P_1=0.50 atm. Assume the contraction ceases when the system reaches equilibrium. Calculate ΔS_{sys}

Solution: $P_2 = 1atm$

$$P_1V_1 = nRT_1 \Rightarrow T_1 = \frac{P_1V_1}{nR} = \frac{\left(0.50atm\right)\left(200L\right)}{\left(5mol\right)\left(0.0821LatmK^{-1}mol^{-1}\right)} = 244K$$

$$\Delta U = nC_v\Delta T = w = -P_{ext}\Delta V$$

$$nC_v\left(T_2 - T_1\right) = nC_v\left(\frac{P_2V_2}{nR} - T_1\right) = -P_{ext}\left(V_2 - V_1\right)$$

$$\therefore V_2\left(P_{ext} + \frac{nC_VP_2}{nR}\right) = nC_VT_1 + P_{ext}V_1$$

$$\therefore V_2 = \left[nC_vT_1 + P_{ext}V_1\right]\left(P_{ext} + \frac{nC_vP_2}{nR}\right)^{-1}$$

$$= \left[(5mol)(1.5)\left(0.0821LatmK^{-1}mol^{-1}\right)(244K) + (1atm)(200L)\right](1atm + 1.5atm)^{-1} = 140L$$

$$T_2 = \frac{P_2V_2}{nR} = \frac{(1atm)(140L)}{(5mol)\left(0.0821L\cdot atm\cdot mol^{-1}\cdot K^{-1}\right)} = 341K$$

$$\Delta S = -nR\ln\left(\frac{P_2}{P_1}\right) + \int_{244K}^{341K}\frac{nC_P}{T}dT = -(5mol)\left(8.314JK^{-1}mol^{-1}\right)\ln\left(\frac{1}{0.5}\right) + (2.5)\left(8.314JK^{-1}mol^{-1}\right)\ln\left(\frac{341}{244}\right)$$

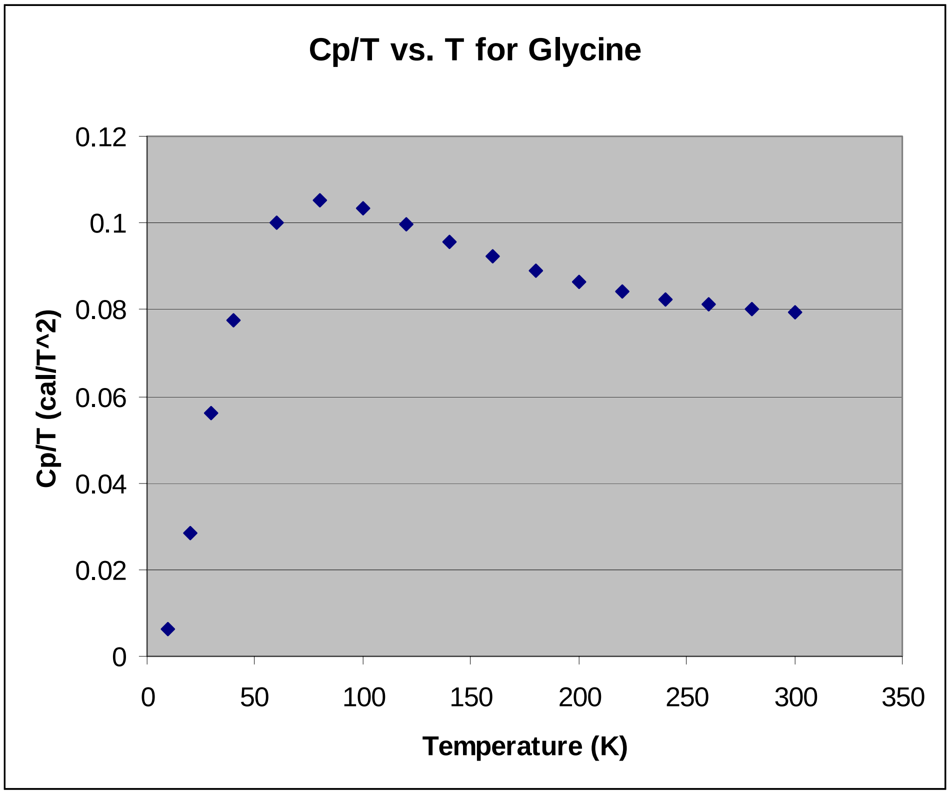
$$= -28.8JK^{-1} + 6.95JK^{-1} = -21.9JK^{-1}$$

5) From the data below, derive the absolute entropy of crystalline glycine at T=298K. Note the heat capacity is in antiquated units…calories per K per mole. There are 4.18J/cal. Give your answer in units of J/Kmole. Hint: Do the necessary calculus graphically, using the fact that an integral is an area under a curve. I want to see a graph of the data from which you get the necessary area. How you get the area accurately is up to you to determine.

Heat Capacity of Crystalline Glycine as a Function of Temperature.

Temperature (K)	Heat Capacity Cp (cal/Kmole)
10	0.061
20	0.572
30	1.682
40	3.108
60	6.012
80	8.427
100	10.34
120	11.95
140	13.40
160	14.74
180	16.02
200	17.28
220	18.52
240	19.80
260	21.14
280	22.48
300	23.84

Solution: Plot Cp/T versus T…The entropy change ΔS is the area under the curve which is
ΔS=26.05 cal/K=108.9J/K.



6) Nitrogen reacts with hydrogen to form ammonia: $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftharpoons NH_3(g)$. The table below gives the standard heats of formation at T=298K and the heat capacities at constant pressure as a function of temperature T:

	$S_f^\circ\left(JK^{-1}mol^{-1}\right)$	$\Delta H^\circ_{f,291K}$ *(kJ mol^{-1})*	$C_P\left(T\right)\left(JK^{-1}mol^{-1}\right)$
$NH_3\left(g\right)$	192.8	-46.1	$25.89+32.58\times10^{-3}\frac{T}{K}-3.046\times10^{-6}\frac{T^2}{K^2}$
$N_2\left(g\right)$	191.6		$26.98+5.912\times10^{-3}\frac{T}{K}-0.3376\times10^{-6}\frac{T^2}{K^2}$
$H_2\left(g\right)$	130.7		$29.07-0.837\times10^{-3}\frac{T}{K}+2.012\times10^{-6}\frac{T^2}{K^2}$

From the data given calculate ΔS_{sys} ,ΔS_{surr} , and $\Delta S_{universe}$ at T=1000K.

$$\Delta S^\circ\left(1000K\right)=\Delta S^\circ\left(298K\right)+\int_{298K}^{1000K}\frac{\Delta C_P^\circ\left(T\right)}{T}dT$$

where from the last problem set:

$$\Delta C_P^\circ\left(T\right)=C_P^\circ\left(NH_3\right)-\tfrac{1}{2}C_P^\circ\left(N_2\right)-\tfrac{3}{2}C_P^\circ\left(H_2\right)=-31.21+30.88\times10^{-3}\frac{T}{K}-5.895\times10^{-6}\frac{T^2}{K^2}$$

$$\Delta S^\circ\left(1000K\right)=\Delta S^\circ\left(298K\right)+\int_{298K}^{1000K}\frac{\Delta C_P^\circ\left(T\right)}{T}dT$$

$$=S^\circ\left(NH_3\right)-\tfrac{1}{2}S^\circ\left(N_2\right)-\tfrac{3}{2}S^\circ\left(H_2\right)+\int_{298K}^{1000K}\left[-\frac{31.21}{T}+30.88\times10^{-3}-5.895\times10^{-6}\frac{T}{K}\right]dT$$

$$=192.8JK^{-1}-\left(0.5\right)\left(191.6JK^{-1}\right)-\left(1.5\right)\left(130.7JK^{-1}\right)$$

$$-\left(31.21JK^{-1}\right)\ln\left(\frac{1000}{298}\right)+\left(30.88\times10^{-3}JK^{-1}\right)\left(1000-298\right)-\left(0.5\right)\left(5.895\times10^{-6}\right)\left(1000^2-298^2\right)$$

$$=192.8JK^{-1}-95.8JK^{-1}-196JK^{-1}-37.8JK^{-1}+21.7JK^{-1}-5.63JK^{-1}=-121JK^{-1}$$

Also from the last problem set:

$$\Delta H_f^\circ\left(1000K\right)=\Delta H_f^\circ\left(298K\right)+\int_{298K}^{1000K}\Delta C_P^\circ\left(T\right)dT=-46.11kJmol^{-1}-9.75kJmol^{-1}=-55.86kJmol^{-1}$$

$$\therefore\Delta S_{surr}=\frac{\Delta H_{surr}}{T_{surr}}=-\frac{\Delta H_{sys}}{T_{surr}}=\frac{55.86kJmol^{-1}}{1000K}=55.86JK^{-1}$$

$$\Delta S_{universe}=\Delta S_{sys}+\Delta S_{surr}=-121JK^{-1}+55.86JK^{-1}=-64.9JK^{-1}$$