Chem 3321 test #1 solutions, out of 60 marks

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

DATA:

R = 0.082 L atm mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}

1 atm = 1.01 × 10^5 Pa = 1.01 bar = 760 torr

1 mL = 1 cm^3

1 Pa = 1 N m^{-2}

0 °C = 273 K

Avogadro's constant = N$_A$ = 6.022 × 10^{23} mol^{-1}

π = 3.14159

1 eV = 1.6022×10^{-19} J (electron volt to joule conversion)

mass conversion from amu to kg: 1.66 × 10^{-27} kg/amu

$C_P - C_V = nR$ for any ideal gas

Problem 1 − 10 marks

One mole of a monoatomic ideal gas initially at T= 400 K and V= 30.0 L has its pressure doubled through a process in which $w = 3.00$ kJ of work is performed on the gas and 0.500 kJ of heat escapes from the gas ($q = -0.500$ kJ).

a) − 5 marks Calculate the final temperature, pressure, and volume of the gas.

Solution: $q + w = 2.5$ kJ $= \Delta U = \frac{3}{2}R\Delta T$ so that $\Delta T = 200$ K, giving T$_2$=600 K.

$$P_1 = \frac{RT_1}{V_1} = 1.093 \text{ atm} \tag{1}$$

so that P$_2$=2.187 atm, and then V$_2$=RT$_2$/P$_2$ = 22.5 L

b) − 2 marks Calculate ΔH for this process.

Solution:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = 4.16 \text{ kJ} \tag{2}$$

c) − 3 marks Why is $q \neq \Delta$H ? Under what conditions are they equal?

Solution: P is not constant. Need constant pressure for them to be equal.

Problem 2 – 20 marks

Consider the following gas phase chemical reaction

$$2\,\mathrm{NO_2}(g) \to \mathrm{N_2O_4}(g) \tag{3}$$

which occurs at a constant pressure of 1.00 bar and at a temperature of either $T = 298$ K or $T = 350$ K. The following data is available:

$T = 298$ K	$\mathrm{NO_2}(g)$	$\mathrm{N_2O_4}(g)$
ΔH_f° (kJ mol^{-1})	33.85	9.66
S° (J K^{-1} mol^{-1})	240.5	304.3
C_P° (J K^{-1} mol^{-1})	37.62	77.24

a) – 2 marks Calculate ΔH_rxn, which is the ΔH for (3), at $T = 298$ K.

Solution:

$$\Delta H_\mathrm{rxn} = \Delta H_f^\circ(\mathrm{N_2O_4}) - 2\Delta H_f^\circ(\mathrm{NO_2}) = -58.04\,\mathrm{kJ} \tag{4}$$

b) – 2 marks Calculate ΔS_rxn, which is the ΔS for (3), at $T = 298$ K.

Solution:

$$\Delta S_\mathrm{rxn} = S^\circ(\mathrm{N_2O_4}) - 2S^\circ(\mathrm{NO_2}) = -176.7\,\mathrm{J\,K^{-1}} \tag{5}$$

c) – 5 marks Calculate ΔH_rxn, which is the ΔH for (3), at $T = 350$ K.

Solution:

We need to construct a thermodynamic cycle as shown in Fig. 1 because this is the only way to answer the question with the given data.

Branch 1 of the path shown in Fig. 1 contributes

$$\Delta H_1 = 2 \int_{350\,\mathrm{K}}^{298\,\mathrm{K}} C_P(\mathrm{NO_2})\,dT = -2 \int_{298\,\mathrm{K}}^{350\,\mathrm{K}} C_P(\mathrm{NO_2})\,dT = -3.9125\,\mathrm{kJ} \tag{6}$$

Branch 2 was calculated in part (a). Branch 3 contributes

$$\Delta H_3 = \int_{298\,\mathrm{K}}^{350\,\mathrm{K}} C_P(\mathrm{N_2O_4})\,dT = 4.0165\,\mathrm{kJ} \tag{7}$$

2
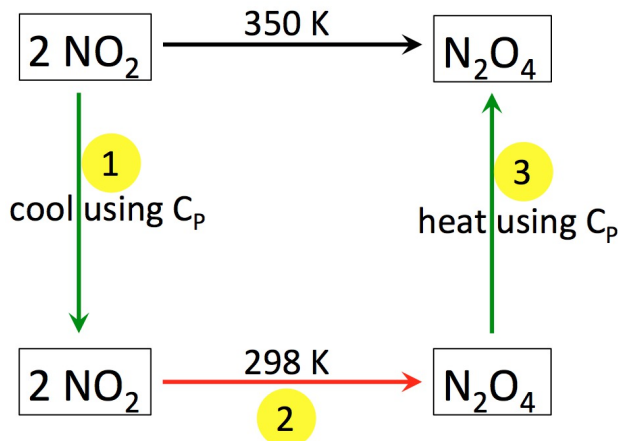
FIG. 1: Thermodynamic cycle. If we follow steps 1, 2, and 3, this is equivalent to following the top 350 K arrow.

Therefore ΔH_{rxn} at $T = 350$ K = -57.94 kJ.

d) − 5 marks Calculate ΔS_{rxn}, which is the ΔS for (3), at $T = 350$ K.

Solution:

Again using the thermodynamic cycle shown in Fig. 1,

$$\Delta S_1 = 2 \int_{350\,\text{K}}^{298\,\text{K}} \frac{C_P(\text{NO}_2)}{T} \, dT = -2 \int_{298\,\text{K}}^{350\,\text{K}} \frac{C_P(\text{NO}_2)}{T} \, dT = -12.10 \, \text{J K}^{-1} \tag{8}$$

Branch 2 was calculated in part (b). Branch 3 contributes

$$\Delta S_3 = \int_{298\,\text{K}}^{350\,\text{K}} \frac{C_P(\text{N}_2\text{O}_4)}{T} \, dT = 12.42 \, \text{J K}^{-1} \tag{9}$$

Therefore ΔS_{rxn} at $T = 350$ K = -176.4 J K^{-1}.

e) − 3 marks Calculate $\Delta S_{\text{surroundings}}$ and $\Delta S_{\text{universe}}$ for (3), at $T = 298$ K. Assume that the surroundings are also at $T = 298$ K. Based on these calculations, will the reaction shown in (3) occur spontaneously under these conditions?

Solution:

Since we are at constant pressure, $q = \Delta H$ (see problem 1c), and $\Delta S_{\text{surroundings}} = -q/T = 194.76$ J K^{-1}. Therefore $\Delta S_{\text{universe}} = -176.7 + 194.8 = 18.1$ J K^{-1}. Since $\Delta S_{\text{universe}} > 0$ this reaction is spontaneous.

f) − 3 marks Calculate $\Delta S_{\text{surroundings}}$ and $\Delta S_{\text{universe}}$ for (3), at $T = 350$ K. Assume that the surroundings are also at $T = 350$ K. Based on these calculations, will the reaction shown in (3) occur spontaneously under these conditions?

Solution:

Since we are at constant pressure, $q = \Delta H$, and $\Delta S_{\text{surroundings}} = -q/T = 165.54 \, \text{J K}^{-1}$. Therefore $\Delta S_{\text{universe}} = -176.4 + 165.5 = -10.9 \, \text{J K}^{-1}$. Since $\Delta S_{\text{universe}} < 0$ this reaction is not spontaneous.

Problem 3 – 15 marks

Data:

	$\bar{S}^\circ$ (J K^{-1} mol^{-1})	$\bar{H}_f^\circ$ (kJ mol^{-1})	density (g cm^{-3})
C(solid,graphite)	5.740	0	2.25
C(solid,diamond)	2.377	2.900	3.51

a) – **5 marks** Graphite and diamond are two forms of solid carbon. Can graphite spontaneously convert to diamond at 25 °C at 1 bar?

Solution: Our criteria for spontaneity at constant temperature and constant pressure is that the Gibbs energy should be negative.

$$\Delta G = \Delta H - T \, \Delta S = [2900 - (298 \times (-3.363))]\text{J/mol} = 3.9\text{kJ/mol} \tag{10}$$

Can not spontaneously convert to diamond because $\Delta G > 0 \Rightarrow$ therefore the reaction is non$-$ spontaneous at $25\,^\circ$C and 1 bar

b) – **5 marks** What is the minimum pressure (in bar) necessary to make this reaction spontaneous?

$$\Delta V = \bar{V}_d - \bar{V}_g = -1.91453 \, cm^3/mol \tag{11}$$
$$\left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow \Delta G = V \, \Delta P \tag{12}$$

Can draw a thermodynamic cycle and apply Hess's law,

$$\Delta G(P) = 0 = 3.9 \, kJ + (P - 1)(-1.91453 \, cm^3/mol) \tag{13}$$
$$P = \frac{-3.9 \times 10^3 \, J/mol \times 0.082 \, Latm \times 1 \, cm^3 \times 1000 \, mL \times 1.01 \, bar}{-1.91453 \, cm^3/mol \times 8.314 \, J \times 1 \, mL \times 1 \, L \times 1 \, atm} + 1bar \tag{14}$$
$$P = 20293 \, bar \tag{15}$$

c) – **5 marks** Will increasing the temperature favor this conversion?

$\Delta G = \Delta H - T\Delta S$ and $\Delta H > 0$ and $\Delta S < 0$, therefore $-T\Delta S > 0$. So when you raise the temperature you will get a more positive ΔG. (Try it : put T = 350 K to get 4.08 kJ). Therefore less favorable at increased temperature.

<u>Problem 4</u> − 5 marks

In Chapter 22 we introduced the Helmholtz and Gibbs energies as new state functions. Why? What are they useful for?

Solution:

We use the Helmholtz energy to determine the direction of a spontaneous reaction at constant T and V and the Gibbs energy to determine the direction of a spontaneous reaction at constant T and P without referring to the surroundings. In both cases the direction of spontaneity is the one which lowers the free energy.

Problem 5 − 10 marks

Prove that for any substance

$$\left(\frac{\partial(A/T)}{\partial T}\right)_V = -\frac{U}{T^2} \tag{16}$$

Solution:

There are several ways this can be done. One approach is as follows:

$$A = U - TS \tag{17}$$

$$A/T = U/T - S \tag{18}$$

$$\left(\frac{\partial A/T}{\partial T}\right)_V = -\frac{U}{T^2} + 1/T\left(\frac{\partial U}{\partial T}\right)_V - \left(\frac{\partial S}{\partial T}\right)_V \tag{19}$$

Since,

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \tag{20}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \times \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{1}{T}\right)_V \times C_V \left[\text{Because } \left(\frac{\partial U}{\partial S}\right)_V = T\right] \tag{21}$$

Therefore

$$\left(\frac{\partial A/T}{\partial T}\right)_V = -\frac{U}{T^2} + \frac{C_V}{T} - \frac{C_V}{T} = -\frac{U}{T^2} \tag{22}$$