Chemistry 366
Thermodynamics
Midterm Exam
April 17, 2008

Name __Key_____

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This is a closed book exam, and you are responsible to be sure that your exam has no missing pages 5 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

But surely this is an old tale you tell, they say;
But surly this is a new tale you tell, other say.
Tell it once again, they say;
Or, do not tell it yet again, others say.
But I have heard all this before, say some;
Or, but this is not how it was before, say the rest

Naqshbandi recital, from The Way of the Sufi, by Idries Shah

Once you start the exam, you have up to 1 hours to solve it.

Honor Statement

I have neither give nor received aid in this examination.

Full signature _____epl_____

PROBLEM 1 (25 POINTS)

A 25.0 g mass of ice at 273 K is added to 150.0 g of $H_2O(l)$ at 360 K at constant pressure. Is the final state of the system ice or liquid water? Calculate ΔS for the process. Is the process spontaneous?

Assume initially that the final state is water. If this is not the case, the calculated temperature will be below 273 K. Calculate ΔS for the ice and water separately, and add them to get the overall ΔS for the process.

$$n_{ice}\Delta H_{fusion}^{ice} + n_{ice}C_{P,m}^{H_2O}\left(T_f - T_i^{ice}\right) + n_{H_2O}C_{P,m}^{H_2O}\left(T_f - T_i^{H_2O}\right) = 0$$

$$T_f = \frac{n_{ice}C_{P,m}^{H_2O}T_i^{ice} + n_{H_2O}C_{P,m}^{H_2O}T_i^{H_2O} - n_{ice}\Delta H_{fusion}^{ice}}{n_{ice}C_{P,m}^{H_2O} + n_{H_2O}C_{P,m}^{H_2O}} =$$

$$\frac{\dfrac{25.0\text{ g ice}}{18.02\text{ g ice mol}^{-1}}\times 75.291\text{ J K}^{-1}\text{mol}^{-1}\times 273\text{ K} + \dfrac{150\text{ g H}_2\text{O}}{18.02\text{ g H}_2\text{O mol}^{-1}}\times 75.291\text{ J K}^{-1}\text{mol}^{-1}\times 360\text{ K}}{}$$

$$\frac{-\dfrac{25.0\text{ g ice}}{18.02\text{ g ice mol}^{-1}}\times 6008\text{ J mol}^{-1}}{\dfrac{25.0\text{ g ice}}{18.02\text{ g ice mol}^{-1}}\times 75.291\text{ J K}^{-1}\text{mol}^{-1} + \dfrac{150\text{ g H}_2\text{O}}{18.02\text{ g H}_2\text{O mol}^{-1}}\times 75.291\text{ J K}^{-1}\text{mol}^{-1}}$$

$$T_f = 336\text{ K}$$

ΔS is calculated for the ice. It consists of melting the ice at 273 K and heating the resulting water to 336 K.

$$\Delta S = n\frac{\Delta H_{fusion}}{T_{fusion}} + nC_{P,m}\ln\frac{T_f}{T_{fusion}}$$

$$= \frac{25.0\text{ g ice}}{18.02\text{ g ice mol}^{-1}}\times\frac{6008\text{ J mol}^{-1}}{273\text{ K}} + \frac{25.0\text{ g ice}}{18.02\text{ g ice mol}^{-1}}\times 75.291\text{ J K}^{-1}\text{mol}^{-1}\ln\frac{336\text{ K}}{273\text{ K}}$$

$$= 30.5\text{ J K}^{-1} + 21.7\text{ J K}^{-1} = 52.2\text{ J K}^{-1}$$

ΔS is calculated for the water. It consists of cooling the water from 360 K to 336 K.

$$\Delta S = nC_{P,m}\ln\frac{T_f}{T_{fusion}} = \frac{150.0\text{ g}}{18.02\text{ g mol}^{-1}}\times 75.291\text{ J K}^{-1}\text{mol}^{-1}\times\ln\frac{336\text{ K}}{360\text{K}} = -43.2\text{ J K}^{-1}$$

$\Delta S_{total} = 0 + 52.2\text{ J K}^{-1} - 43.2\text{ J K}^{-1} = 9.0\text{ J K}^{-1}$. The process is spontaneous.

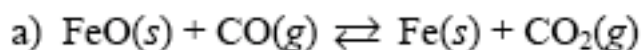**PROBLEM 2 (25 POINTS)**

Consider the reaction $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ for which K_p is found to have the following values:

T	600°C	1000°C
K_p	0.900	0.396

a) Calculate $\Delta G^\circ_{reaction}$, $\Delta S^\circ_{reaction}$ and $\Delta H^\circ_{reaction}$ for this reaction at 600°C. Assume that $\Delta H^\circ_{reaction}$ is independent of temperature.

b) Calculate the mole fraction of $CO_2(g)$ present in the gas phase at 600°C.

a) $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

$$K_P = \frac{P_{CO_2}/P^\circ}{P_{CO}/P^\circ}$$

$$\ln \frac{K_P(1000°C)}{K_P(600°C)} = \frac{\Delta H^\circ_{reaction}}{R}\left(\frac{1}{1273.15 \text{ K}} - \frac{1}{873.15 \text{ K}}\right)$$

Assume that $\Delta H^\circ_{reaction}$ is independent of temperature.

$$\Delta H^{\circ}_{reaction} = \frac{-R \ln \dfrac{K_P(1000°C)}{K_P(600°C)}}{\left(\dfrac{1}{1273.15 \text{ K}} - \dfrac{1}{873.15 \text{ K}}\right)}$$

$$= \frac{-8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \dfrac{0.0396}{0.900}}{\left(\dfrac{1}{1273.15 \text{ K}} - \dfrac{1}{873.15 \text{ K}}\right)} = -19.0 \text{ kJ mol}^{-1}$$

$$\Delta G^{\circ}_{reaction}(600°C) = -RT \ln K_P(600°C)$$

$$= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 873.15 \text{ K} \times \ln(0.900) = 765 \text{ J mol}^{-1}$$

$$\Delta S^{\circ}_{reaction}(600°C) = \frac{\Delta H^{\circ}_{reaction} - \Delta G^{\circ}_{reaction}(600°C)}{T} = \frac{-18960 \text{ J mol}^{-1} - 765 \text{ J mol}^{-1}}{873.15 \text{ K}} = -22.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

b) because $K_P = P_{CO_2}/P_{CO} = 0.900$

$K_P = K_x$ because $\Delta \nu = 0$

$\dfrac{x_{CO_2}}{x_{CO}} = 0.900$ and $x_{CO_2} + x_{CO} = 1$

$x_{CO_2} = 0.47 \quad x_{CO} = 0.53$

PROBLEM 3 (25 POINTS)

For a gas at a given temperature, the compressibility is described by the empirical equation $z = 1 - 9.00 \times 10^{-3} \dfrac{P}{P^\circ} + 4.00 \times 10^{-5} \left(\dfrac{P}{P^\circ}\right)^2$, where $P^\circ = 1$ bar.

Calculate the activity coefficient for

P=300 K

$$\ln \gamma = \int_0^P \frac{z-1}{P'} dP' = \int_0^P \frac{\left(1 - 9.00 \times 10^{-3} P' + 4.00 \times 10^{-5} (P')^2\right) - 1}{P'} dP'$$

$$\ln \gamma = -9.00 \times 10^{-3} P + 2.00 \times 10^{-5} P^2$$

$\gamma = 0.497, 0.368, 0.406, 0.670,$ and 1.65 at $100, 200, 300, 400,$ and 500 bar, respectively.

PROBLEM 4 (25 POINTS)

The vapor pressure of methanol (l) is given by $\ln\left(\dfrac{P}{Pa}\right) = 23.593 - \dfrac{3.6791\times10^3}{\dfrac{T}{K}-31.317}$.

a) Calculate the standard boiling temperature.
b) Calculate $\Delta H_{vaporization}$ at 298 K and at the standard boiling temperature.

a)

$$\ln\left(\frac{P}{Pa}\right) = 23.593 - \frac{3.6791\times10^3}{\frac{T_b}{K}-31.317} = \ln 10^5 = 11.5129$$

$$3.6791\times10^3 = (23.593-11.5129)\left(\frac{T_b}{K}-31.317\right)$$

$$\frac{T_b}{K} = \frac{3.6791\times10^3}{(23.593-11.5129)}+31.317 = 335.9$$

b)

$$\Delta H_{vaporization} = RT^2\frac{d\ln P}{dT} = \frac{8.314 \text{ J mol}^{1}\text{ K}^{-1}\times3679.1\times(298\text{ K})^2}{(T-31.37)^2}$$

$$= 38.19 \text{ kJ mol}^{-1} \text{ at 298 K and } 37.20 \text{ kJ mol}^{-1} \text{ at 335.9 K}$$