## Chemistry 2000 Fall 2013 Test 2 Version A

1. We need T in K:

$$T = 20 + 273.15 = 293.15 \,\mathrm{K}.$$

The atomic mass unit is numerically equal to the  $g \mod^{-1}$ , but we need kg  $\mod^{-1}$  in the rms speed formula, so the relevant molar mass is

$$M = 0.222 \,0176 \,\mathrm{kg \, mol^{-1}}.$$

From here, the calculation is straightforward:

$$v_{\rm rms} = \sqrt{\frac{3RT}{M}}$$
  
=  $\sqrt{\frac{3(8.3145 \,\mathrm{J}\,\mathrm{K}^{-1}\mathrm{mol}^{-1})(293.15 \,\mathrm{K})}{0.222 \,0176 \,\mathrm{kg}\,\mathrm{mol}^{-1}}}$   
= 181 m s<sup>-1</sup>.

2. The second law states that the entropy change of the *universe* must be positive. The entropy of reaction is only one component. The other is the entropy change of the surroundings. Assuming that the surroundings are relatively unaffected by the reaction, we have

$$\Delta S_{\rm surr} = \frac{q_{\rm surr}}{T_{\rm surr}} = -\frac{q_r}{T_{\rm surr}}$$

where  $q_r$  is the heat of reaction. If this heat is negative, i.e. if the reaction is exothermic, then  $\Delta S_{\text{surr}}$  is positive. The reaction can still be allowed by the second law if  $\Delta S_{\text{surr}}$  is larger in absolute value than the negative  $\Delta_r S$ .

- 3. The acetone is pulled up along the tube walls by the larger intermolecular forces between the quartz and acetone than between the acetone molecules.
- 4. The balanced reaction is

$$\mathrm{NO}_{(\mathrm{g})} + \frac{1}{2}\mathrm{O}_{2(\mathrm{g})} \to \mathrm{NO}_{2(\mathrm{g})}.$$

The standard free energy change for this reaction is

$$\Delta_r G^{\circ} = \Delta_f G^{\circ}(\text{NO}_2) - \left[ \Delta_f G^{\circ}(\text{NO}) + \frac{1}{2} \Delta_f G^{\circ}(\text{O}_2) \right]^0$$
  
= 51.32 - 86.60 kJ mol<sup>-1</sup>  
= -35.28 kJ mol<sup>-1</sup>.



Figure 1: Phase diagram of carbon with one possible path that forms diamond from the melt. The two triple points are labeled tp1 and tp2.

Once we have the standard free energy change, we can calculate the actual free energy change under the conditions of the problem:

$$\begin{aligned} \Delta_r G &= \Delta_r G^\circ + RT \ln Q \\ &= \Delta_r G^\circ + RT \ln \left( \frac{a_{\rm NO_2}}{(a_{\rm NO})(a_{\rm O_2})^{1/2}} \right) \\ &= -35.28 \,\text{kJ} \,\text{mol}^{-1} + (8.3145 \times 10^{-3} \,\text{kJ} \,\text{K}^{-1} \text{mol}^{-1})(298.15 \,\text{K}) \ln \left( \frac{0.0032}{(0.0041)(0.21)^{1/2}} \right) \\ &= -33.96 \,\text{kJ} \,\text{mol}^{-1}. \end{aligned}$$

Since the free energy change is negative, the reaction is allowed.

5. Figure 1 shows one possible path that has the desired effect. The phase diagram has two triple points labeled tp1 and tp2.

Starting from point 1:

- (a) Raise the pressure until it exceeds the pressure at tp1, reaching point 2.
- (b) Increase the temperature, melting the graphite and forming the liquid phase at point 3.
- (c) Increase the pressure of the liquid until the pressure exceeds that at tp2, reaching point 4.

(d) Decrease the temperature until diamond has been formed, ending at, say, point 5. Since diamond is metastable at ordinary temperatures and pressures, the diamonds so formed can be returned to ambient temperature and pressure thereafter.

6. (a)

$$\begin{split} \Delta_r G^{\circ} &= \Delta_f G^{\circ}(\mathbf{H}^+) + \Delta_f G^{\circ}(\mathbf{Cl}^-) - \Delta_f G^{\circ}(\mathbf{HCl}) \\ &= -131.218 - (-95.30) \, \mathrm{kJ \, mol^{-1}} \\ &= -35.92 \, \mathrm{kJ \, mol^{-1}}. \\ \Delta_r G^{\circ} &= -RT \ln K \\ \therefore \ln K &= -\frac{\Delta_r G^{\circ}}{RT} \\ \therefore K &= \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) \\ &= \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) \\ &= \exp\left(\left(-\frac{-35.92 \times 10^3 \, \mathrm{J \, mol^{-1}}}{(8.3145 \, \mathrm{J \, K^{-1} mol^{-1}})(298.15 \, \mathrm{K})}\right) \\ &= 1.96 \times 10^6. \end{split}$$

- (b) A strong acid dissociates completely in water. The large value of the equilibrium constant tells us that even gaseous HCl is strongly driven to form solvated ions in the presence of water, which is consistent with the strongly acidic nature of HCl.
- (c) If  $[\text{HCl}] = 12 \text{ mol } \text{L}^{-1}$ , the concentrations of H<sup>+</sup> and Cl<sup>-</sup> ions in solution are each  $12 \text{ mol } \text{L}^{-1}$  since, again, HCl is a strong acid. Thus,  $a_{\text{H}^+} = a_{\text{Cl}^-} = c/c^\circ = 12$ .

The pressure of HCl is related to its activity:  $a_{\rm HCl} = p_{\rm HCl}/p^{\circ}$ . Accordingly,

$$K = \frac{(a_{\rm H^+})(a_{\rm Cl^-})}{a_{\rm HCl}}$$
$$\therefore a_{\rm HCl} = \frac{(a_{\rm H^+})(a_{\rm Cl^-})}{K}$$
$$= \frac{(12)^2}{1.96 \times 10^6} = 7.3 \times 10^{-5}.$$

Since  $p^{\circ} = 1$  bar, this gives  $p_{\rm HCl} = 7.3 \times 10^{-5}$  bar.

7. (a) For a liquid, a = X. The percentages are of course just an alternative way of expressing mole fractions, so we have  $X_1 = 0.3479$ ,  $X_2 = 0.3510$  and  $X_3 = 0.3011$ . Thus,

$$K_A = \frac{a_2}{a_1} = \frac{0.3510}{0.3479} = 1.009.$$
$$K_B = \frac{a_3}{a_2} = \frac{0.3011}{0.3510} = 0.8578.$$

(b) We will be using the formula

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H_m^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right),\tag{1}$$

which we can rearrange to solve to  $\Delta_r H_m^{\circ}$ . Choose  $T_1 = 235 \,^{\circ}\text{C} \equiv 508.15 \,\text{K}, \quad K_1 = 1.009;$  $T_2 = 265 \,^{\circ}\text{C} \equiv 538.15 \,\text{K}, \quad K_2 = 4.665.$ 

We can go straight into equation 1:

$$\Delta_r H_m^{\circ} = \frac{R \ln(K_2/K_1)}{\frac{1}{T_1} - \frac{1}{T_2}}$$
  
=  $\frac{(8.3145 \,\mathrm{J}\,\mathrm{K}^{-1}\mathrm{mol}^{-1})\ln(4.665/1.009)}{\frac{1}{508.15 \,\mathrm{K}} - \frac{1}{538.15 \,\mathrm{K}}}$   
= 116 kJ mol<sup>-1</sup>.

The first reaction is endothermic.

(c)

$$\Delta_r G^\circ = -RT \ln K$$
  
= -(8.3145 J K<sup>-1</sup>mol<sup>-1</sup>)(298.15 K) ln (4.00 × 10<sup>-9</sup>)  
= 47.9 kJ mol<sup>-1</sup>.

(d) We know  $\Delta_r H^\circ$  and  $\Delta_r G^\circ$ , so we can solve for  $\Delta_r S^\circ$  from

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ.$$
  
$$\therefore \Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T}$$
$$= \frac{116 - 47.9 \text{ kJ mol}^{-1}}{298.15 \text{ K}}$$
$$= 0.23 \text{ kJ K}^{-1} \text{mol}^{-1}.$$

Compound 2 has the higher entropy.