Problem Set #2   Chem 471   Fall 1999

Due Friday, 9/24/99, in class.

Show your work. Problem sets will be spot graded. Work must be shown.

$R = 0.08206$ liter atm K^{-1} mole^{-1} = 8.314 J K^{-1} mole^{-1}

1. Differentiate the following:

     a) $PV = nRT$ P with respect to T

     b) $PV = nRT$ P with respect to V

     c) $z = e^{ax}$ z with respect to x

     d) $q = e^{-Ei/kT}$ q with respect to T

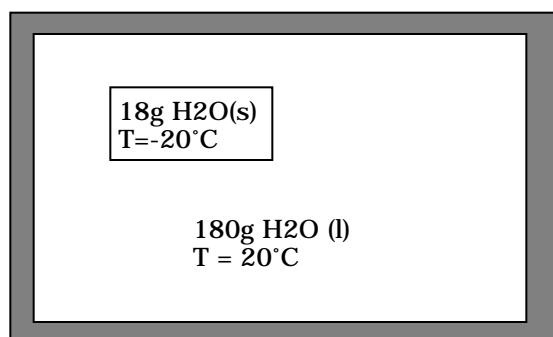   e) $q = $ $e^{-Ei/kT}$ q with respect to T

2. T,S,&W Ch 2 Pb 12

         (a) 18 g ice cube warmed from -20 to 0˚C without melting:

         $q = C_p(T_2-T_1) = C_p(\text{ice})(0+20) = (2.113\text{kJ/kgK})(.018\text{kg})(20\text{K}) = 0.761$ kJ

         (b) 18 g ice cube melting at 0˚C, 1 atm:

         $q = H_{melting} = (6.007\text{kJ/mole})(\text{mole/18g})(18\text{g}) = 6.007\text{kJ}$

         18g H2O(s)
         T=-20˚C

         180g H2O (l)
         T = 20˚C

         thermally insulated --
         q flow all between ice and water

         (c) 18g ice cube (-20˚C) into 180 g water (20˚C) -- what is final state?

         The ice will melt, with V 0 so w=0. Need to determine final temperature of 198g water.

         q gained by ice = q lost by water since container is insulated (no q flow out of system)

         let T_f = final temperature

         q_{ice} = warming -20 to 0 (a) + melting (b) + warming 0 to T_f = 761J + 6007J + C_p(water) T

         q_{ice} = 6768J +(18g)(4.18kJ/kgK)(T_f-273K)

         q_{water} = cooling 20 to T_f = C_p(water) T = (180g)(4.18kJ/kgK)(T_f-293K)

         q_{ice} = -q_{water} note kJ/kg = J/g

         6768J + (75.2 J/K)(T_f-273K) = -(752 J/K)(T_f-293K)

         6768J - 20529.6J - 220336J = -T_f(752+75.2)J/K

         (-234097.6J)/(827.2J/K) = -T_f

$T_f = 283K = 10 \, °C$

Final state is 198g liquid water at 10°C.

3. T,S,&W Ch 2 Pb 24

$CH_3OH(l) \quad CH_4(g) + 1/2 \, O_2(g)$

(a) $\quad H^0(298) = H_f(CH_4(g)) + (1/2) \, H_f(O_2(g)) - H_f(CH_3OH(l))$

$H^0(298) = -74.81 \, kJ/mole + 0 - (-238.57 \, kJ/mole) = 163.76 \, kJ/mole$

(b) $\quad E^0(298) = H^0(298) - nRT$

$E^0(298) = 163.76 \, kJ/mole - (1.5-0)(8.3145 J/Kmole)(298K)(10^{-3} \, kJ/J)$

$E0(298) = 160.04 kJ/mole$

$$H^0_{773} = H^0_{298} + \int_{298}^{773} C_p dT$$

(c)

$$C_p = C_p(CH_4) + \frac{1}{2} C_p(O_2) - C_p(CH_3OH)$$

4. T,S,&W Ch 2 Pb 35

This is a simple problem. In the same way that the book discusses estimating bond energies from energetics of relevant reactions, this problem is showing that we can estimate the steric energy in cis vs. trans by comparing the energetics of the reaction

$$\text{cis-2-butene} \quad \text{trans-2-butene}$$
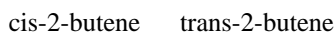
The enthalpy of this is: $(-11.1) - 7.0 = -4.1 \, kJ \, mol^{-1}$

So the trans form is lower in enthalpy by 4 kJ mol^{-1}

5. T,S,&W Ch 3 Pb 9

a) $6 \, C \, (s, \text{graphite}) + 3 \, H_2 \, (g) \quad C_6H_6 \, (g)$
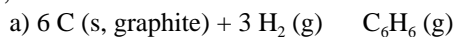
$G°_{298} = G°_{f,298} \, (\text{benzene}) = 129.66 \, kJ \, mol^{-1}$

I would not buy the catalytst. Catalysts cannot change the thermodynamic favorability of a reaction. They can only speed up an otherwise spontaneous process. Consequently, a catalyst can not make this unfavorable reaction favorable.

b) $2 \, NO \, (g) + O_2 \, (g) \quad 2 \, NO_2 \, (g)$
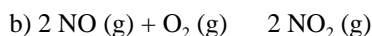
$G°_{298} = -2 \, (86.55) + 0 + 2 \, (51.31) = -70.48 \, kJ \, mol^{-1}$ The reaction is spontaneous.

c) $3 \, CH_4 \, (g) + NH_3 \, (g) + 3 \, O_2 \, (g) \quad CH_3CHNH_2COOH \, (s) + 4 \, H_2O \, (l)$

$G°_{298} = -3 \, (-50.72) - (-16.45) + 0 + (-370.24) + 4 \, (-237.129) = -1150.15 \, kJ \, mol^{-1}$ The reaction is spontaneous.

6. T,S,&W Ch 3 Pb 16

a) The values requested are:

$w = -P_m \, V_m$

$E = q_m + w = q_m - P_m \, V_m$

$H = q_m$

$S = q_m / T_m$

$G = 0$

b) $\quad H = q_m + \left(C_p^\beta - C_p^\alpha \right) \left(T^* - T_m \right)$

$$S = \frac{q_m}{T_m} + \left(C_p^\beta - C_p^\alpha \right) \ln \frac{T^*}{T_m}$$

c) Simply plugging in to equations in (a):

$G = 0$

H = 638 kJ mol^{-1}
S = (638 kJ mol^{-1}) / 343 K = 1.86 kJ K^{-1} mol^{-1}

d) Using equations from (b)
H = 638 kJ mol^{-1} – (8.37 kJ mol^{-1}) (37 - 70) K = 914 kJ mol^{-1}
S = 1.86 kJ K^{-1} mol^{-1} – (8.37 kJ mol^{-1}) ln 310/343 = 2.71 kJ K^{-1} mol^{-1}
G = H - T S = 73.9 kJ mol^{-1}

e) Think this one through. V_m >0 means that volume increases with   . Therefore, increasing pressure will push the reaction to the left (towards the smaller   phase). This will require a higher T_m.

f) We can draw the cycle below:

$$G_{m.Pm}$$

T$_m$,P$_m$ $\longrightarrow$ T$_m$,P$_m$

G $\downarrow$ $\uparrow$ G

T*,1000 $\longrightarrow$ T*,1000
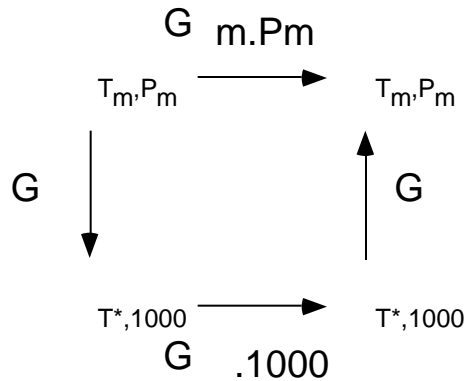
$$G_{.1000}$$

Both phase transitions are said to occur under equilibrium, so that:
$G_{Tm,Pm} = 0$
$G_{T*,1000} = 0$

And from the cycle at left, we have:

$$G_{T_m,P_m} = G_\alpha + G_{T_m,P_m} + G_\beta$$

$$0 = G_\alpha + 0 + G_\beta$$

$$G_\alpha = \int_{P_m}^{1000} V_\alpha dP - \int_{T_m}^{T*} S_\alpha dT = V_\alpha(1000 - P_m) + S_{\alpha,T_m} - C_p^\alpha \ln\frac{T*}{T_m}$$

$$G_\beta = \int_{1000}^{P_m} V_\beta dP - \int_{T*}^{T_m} S_\beta dT = V_\beta(P_m - 1000) - S_{\beta,T_m} - C_p^\beta \ln\frac{T_m}{T*}$$
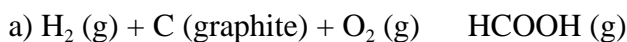
$$0 = V_\alpha(1000 - P_m) + V_\beta(P_m - 1000) - S_{\beta,T_m} + S_{\alpha,T_m} - C_p^\alpha \ln\frac{T*}{T_m} - C_p^\beta \ln\frac{T_m}{T*}$$

$$0 = (V_\beta - V_\alpha)(P_m - 1000) - S_{T_m} + (C_p^\beta - C_p^\alpha)\ln\frac{T*}{T_m}$$

$$0 = V(P_m - 1000) - S_{T_m} - C_p \ln\frac{T_m}{T*}$$

From this, we can solve for T*

7. T,S,&W Ch 3 Pb 18
   a) H$_2$ (g) + C (graphite) + O$_2$ (g)   HCOOH (g)

   b) H° = -785.34 - 2(-362.63) = –60.08 kJ mol^{-1}
      S° = 347.7 – 2(251.0) = –154.3 kJ K^{-1} mol^{-1}

$G° = -60.08 \text{ kJ mol}^{-1} - (298 \text{ K})(-0.1543 \text{ kJ K}^{-1} \text{ mol}^{-1}) = -14.1 \text{ kJ mol}^{-1}$

c) $H°$ (single H-bond) = -60.08/2 = -30.04 kJ mol^{-1}
The entropy change involves changes in both translational and rotational entropy. It is not simple to separate these, as it is the H-bond enthalphy.

Extra - don't turn in - think about the questions posed in Ch 3 Pb 22.