Chem 531: Problem Set #9 **SOLUTIONS**

Due in class: Thursday, December 7th

(1) Consider the equilibrium $C_2H_6(g) \rightleftarrows C_2H_4(g) + H_2(g)$. At 1000 K and a constant total pressure of 1 bar, $C_2H_6(g)$ is introduced into a reaction vessel. The total pressure is held constant at 1 bar and at equilibrium the composition of the mixture in mole percent is $H_2(g)$: 26%, $C_2H_4(g)$: 26%, and $C_2H_6(g)$: 48%.

(a) Calculate K_P at 1000 K.

(b) If ΔH_r° = 137.0 kJ/mol, estimate the value of K_P at 298.15 K.

(c) Calculate ΔG_r° for this reaction at 298.15 K.

a) at 1000 K, equil. composition is:

(all mole percents)		x_i
26%	H_2	0.26
26%	C_2H_4	0.26
48%	C_2H_6	0.48

in each case, $P_i = x_i P$ where $P = 1$ bar

$$K_p = \frac{\left(P_{C_2H_4}/P^\circ\right)\left(P_{H_2}/P^\circ\right)}{\left(P_{C_2H_6}/P^\circ\right)} = \frac{(0.26)(0.26)}{0.48} \cdot \frac{1}{P^\circ}$$

$$= 0.1408$$

b) integrated van't Hoff eqn:

$$\ln K_p(298.15) = \ln K_p(1000) - \frac{\Delta H_r^\circ}{R}\left(\frac{1}{298.15} - \frac{1}{1000}\right)$$

$$= \ln(0.1408) - \frac{137 \times 10^3}{8.3145}\left(\frac{1}{298.15} - \frac{1}{1000}\right)$$

$$= -40.75$$

$$K_p(298.15\ K) = 2.01 \times 10^{-18}$$

c) $\Delta G_r^\circ = -RT\ln K_p = -(8.3145)(298.15)(-40.75)$

$$= 101\ kJ/mol$$

(2) The following data apply to the reaction $Br_2(g) \rightleftarrows 2Br(g)$:

T (in K)	1123	1172	1223	1273
K_P	0.408×10^{-3}	1.42×10^{-3}	3.32×10^{-3}	7.2×10^{-3}

Determine by graphical means the reaction enthalpy at 1200 K.

at const. P, $\dfrac{d \ln K_p}{dT} = \dfrac{\Delta H_r^\circ}{RT^2}$

Strategy: obtain analytical form for $\ln K_p(T)$ by fitting to polynomial in T. then take derivative at $T = 1200$ K, which gives $\dfrac{\Delta H_r^\circ}{RT^2}$.

see accompanying plot.

$\ln K_p(T) = -972.0101 + 2.32724\,T - 0.0018797\,T^2 + 5.09311 \times 10^{-7} T^3$

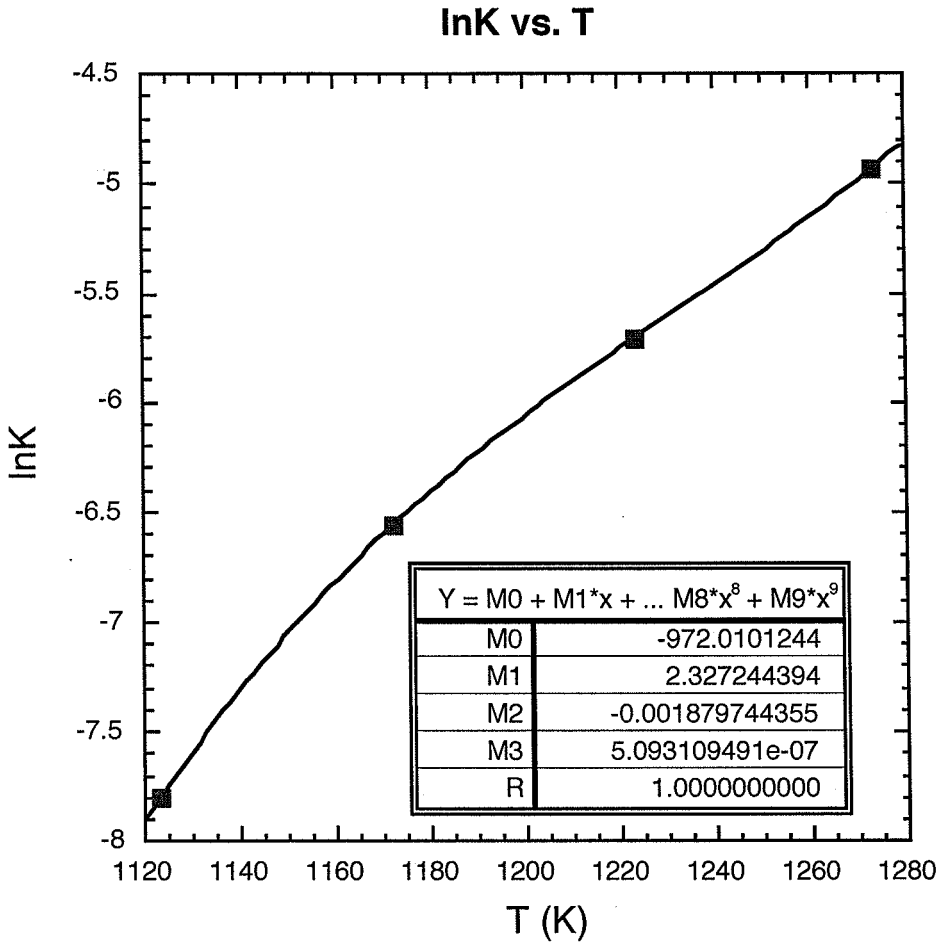
$\dfrac{d \ln K_p}{dT} = 2.32724 - 0.0037594\,T + 1.5279 \times 10^{-6} T^2$

at $T = 1200$K, $\dfrac{d \ln K_p}{dT} = 1.61835 \times 10^{-2}$

$\Delta H_r^\circ = RT^2 \left(\dfrac{d \ln K_p}{dT} \right) = (8.3145)(1200)^2 (1.61835 \times 10^{-2})$

$= 193,763$ J/mol

$= 194$ kJ/mol


lnK vs. T
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
lnK
1120
1140
1160
1180
1200
1220
1240
1260
1280
T (K)
Y = M0 + M1*x + ... M8*x^8 + M9*x^9
M0 -972.0101244
M1 2.327244394
M2 -0.001879744355
M3 5.093109491e-07
R 1.0000000000