Chem 402—Physical Chemistry
Homework Problem Set—Chapter 24

Due Tuesday, Mar. 4, 2008

1. For the thermal decomposition of F_2O by the reaction $2\ F_2O(g) \rightarrow 2\ F_2(g) + O_2(g)$, the following mechanism has been suggested:

$F_2O + F_2O \rightarrow F + OF + F_2O$	k_1
$F + F_2O \rightarrow F_2 + OF$	k_2
$OF + OF \rightarrow O_2 + F + F$	k_3
$F + F + F_2O \rightarrow F_2 + F_2O$	k_4

   (a) Using the steady-state approximation, show that this mechanism is consistent with the experiemntal rate law

   $$-\frac{d[F_2O]}{dt} = k[F_2O] + k'[F_2O]^{3/2}$$

   (b) The experimentally determined Arrhenius parameters in the range 501 – 583 K are A = 7.8×10^{13} L mol^{-1} s^{-1}, $E_a/R = 1.935 \times 10^4$ K for k and A = 2.3×10^{10} L mol^{-1} s^{-1}, $E_a/R = 1.691 \times 10^4$ K for k'. At 540 K, $\Delta_f H^o(F_2O) = 24.41$ kJ mol^{-1}, D(F-F) = 160.6 kJ mol^{-1}, and D(O-O) = 498.2 kJ mol^{-1}. (D = bond dissociation energy) Estimate the bond dissociation energies of the first and second F-O bonds and the Arrhenius activation energy of reaction 2.

2. For the gas phase reaction $A + A \rightarrow A_2$, the experimental rate coefficient can be expressed as:

   $k_2 = (4.07 \times 10^5\ \text{L mol}^{-1}\ \text{s}^{-1}) \exp\{-65.43\ \text{kJ mol}^{-1}/RT\}$

   Calculate ΔS^*, ΔH^*, ΔU^*, and ΔG^* for the reaction.

3. The gas phase reaction $2\ HI \rightarrow H_2 + I_2$ has measured rate coefficients in the forward (k) and reverse (k') directions as follows:

T (K)	647	666	683	700	716	781
k/(22.4 L mol^{-1} min^{-1})	0.230	0.588	1.37	3.10	6.70	105.9
k'/(22.4 L mol^{-1} min^{-1})	0.0140	0.0379	0.0659	0.172	0.375	3.58

   Demonstrate that these data are consistent with the collision theory of bimolecular gas phase reactions.

4. For the reaction $NO(g) + Cl_2(g) \rightarrow NOCl(g) + Cl(g)$, calculate the hard-sphere collision theory rate coefficient. Collision diameters are: NO, d = 370 pm; Cl_2, d = 540 pm. The Arrhenius equation for this reaction is

   $k(T) = (3.981 \times 10^9\ \text{L mol}^{-1}\ \text{s}^{-1}) \exp\{-84.9\ \text{kJ mol}^{-1}/RT\}$

   Calculate the ratio of the collision theory rate coefficient to the experimental rate coefficient at 300 K.