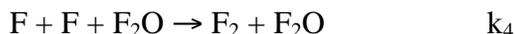
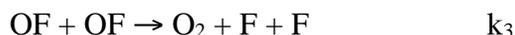


Chem 402—Physical Chemistry
Homework Problem Set—Chapter 24

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:



- (a) Using the steady-state approximation, show that this mechanism is consistent with the experimental 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 $A = 7.8 \times 10^{13} \text{ L mol}^{-1} \text{ s}^{-1}$, $E_a/R = 1.935 \times 10^4 \text{ K}$ for k and $A = 2.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, $E_a/R = 1.691 \times 10^4 \text{ K}$ for k' . At 540 K, $\Delta_f H^\circ(F_2O) = 24.41 \text{ kJ mol}^{-1}$, $D(F-F) = 160.6 \text{ kJ mol}^{-1}$, and $D(O-O) = 498.2 \text{ kJ mol}^{-1}$. (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^\ddagger , ΔH^\ddagger , ΔU^\ddagger , and ΔG^\ddagger 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
$k/(22.4 \text{ L mol}^{-1} \text{ min}^{-1})$	0.230	0.588	1.37	3.10	6.70	105.9
$k'/(22.4 \text{ L mol}^{-1} \text{ min}^{-1})$	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, $d = 370 \text{ pm}$; Cl_2 , $d = 540 \text{ pm}$. 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.