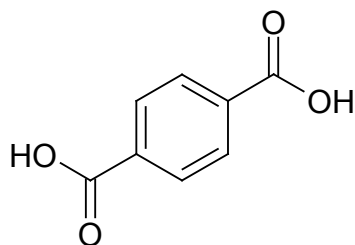


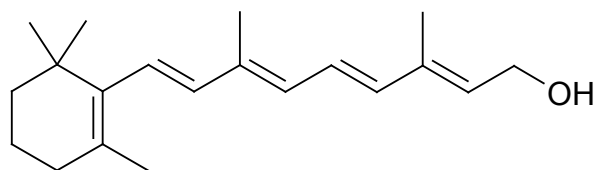
CE 561 Homework 7: (assigned 10/14/09, due 10/19/09)

- (1) For the organic compounds given by the following two structures, give the common name for the compound, name an application for which it is used, and make a group additivity estimate of the heat of formation and standard entropy at 298 K. Note that the group additivity estimates are for *gas phase* thermochemical properties. Literature data for these compounds may be for the liquid or solid phase.

(a)



(b)



- (2) The recombination of iodine atoms ($2 \text{I} \rightarrow \text{I}_2$) in a particular solvent is believed to be diffusion controlled. At 298 K, the rate constant is observed to be 1.3×10^{10} liter mole⁻¹ s⁻¹.

- (a) If the reaction distance (r_{AB}) is taken to be 2.2 \AA , estimate the diffusion coefficient of I atoms in this solvent at 298 K.
- (b) The temperature dependence of diffusion coefficients in liquids is roughly given by $D = D_0 \left(\frac{T}{\mu} \right)$ where μ is the (temperature dependent) viscosity of the solvent.

The viscosity of the solvent vs. temperature is

T (°C)	μ (cP)
0	0.581
20	0.326
40	0.214
60	0.154
80	0.119
100	0.096

Make an Arrhenius plot of the rate constant for the $\text{I} + \text{I}$ reaction for temperatures from 273 to 373 K. What is the apparent activation energy for this diffusion controlled reaction?

- (3) For some hypothetical reaction between two neutral molecules in solution, $A+B \rightarrow$ products, the measured rate coefficient vs. temperature is

T(K)	273	278	283	288	293	298	303
k (liter mole ⁻¹ s ⁻¹)	8.67E+08	1.57E+09	2.70E+09	4.37E+09	6.62E+09	9.41E+09	1.26E+10
T(K)	308	313	318	323	328	333	338
k (liter mole ⁻¹ s ⁻¹)	1.60E+10	1.95E+10	2.31E+10	2.66E+10	3.00E+10	3.34E+10	3.68E+10
T(K)	343	348	353	358	363	368	373
k (liter mole ⁻¹ s ⁻¹)	4.02E+10	4.35E+10	4.68E+10	5.01E+10	5.34E+10	5.66E+10	5.98E+10

An Arrhenius plot of this data shows strong curvature that indicates a transition from reaction-limited behavior at lower temperatures to diffusion-controlled behavior at higher temperatures. The diffusion coefficients of A and B in the solvent at 298 K are known to be $3.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively. Extract from the data given above values for the reaction distance for diffusion controlled reaction (r_{AB}) and the activation energy and pre-exponential factor for k_R , the rate constant that would be measured in the absence of any diffusion limitations. ***The solvent in this problem is the same as that in problem (2), so you have information about the temperature dependence of the diffusion coefficients from part (b) of problem (2).***