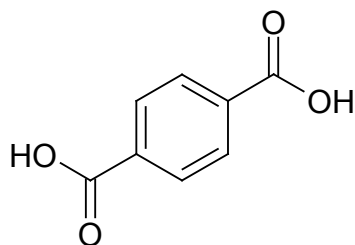


CE 561 Homework 6: (solutions in blue)

- (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)



This is terephthalic acid. It is an intermediate in polyester synthesis. It is made by catalytic partial oxidation of para-xylene, which is separated from crude oil. It contains 4 CB-(H) groups, two CB-(CO) groups, two CO-(CB)(O) groups, and two O-(CO)(H) groups. Constructing the group additivity estimate manually, using the tables provided in the lecture notes, gives:

Group	Quantity	H group value (kcal/mol)	H contribution (kcal/mol)	S group value (cal/(mol K))	S contribution (cal/(mol K))
CB-(H)	4	3.30	13.20	11.53	46.12
CB-(CO)	2	3.69	7.38	-7.80	-15.60
CO-(CB)(O)	2	-36.60	-73.20	14.78	29.56
O-(CO)(H)	2	-58.10	-116.20	24.50	49.00
		Total	-168.82		109.08

So, this manual group additivity estimate for the heat of formation is -169 kcal/mol, and the corresponding group additivity estimate for the standard entropy at 298 K is 109 cal mol⁻¹ K⁻¹.

Using the group additivity calculator on the NIST web site gives:

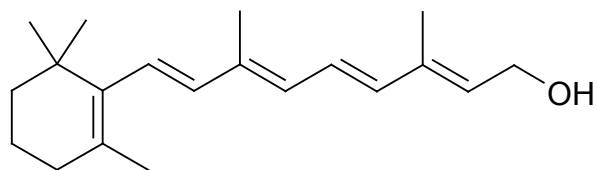
Results

Quantity	Value
$\Delta_f H^\circ_{\text{gas,est}}$ (kcal/mol)	-162.8
$S^\circ_{\text{gas,est}}$ (cal/mol*K)	107.19

Both estimates are a little different from what was obtained by hand. The group values used by the NIST site for the CO-(CB)(O) group are a little different from those in the tables. It also applies a symmetry correction for the entropy that the manual calculation left out.

The NIST chemistry webbook gives the experimental heat of formation for the solid as -195 kcal/mol. It also gives the standard heat of sublimation as 23.5 kcal/mol, so the gas phase heat of formation is -171.6 kcal/mol. The group additivity estimate is quite close to this.

(b)



This is vitamin A. In your eye it is converted to cis-retinal, which in turn reacts with opsin (a protein) to form rhodopsin. The piece of the rhodopsin that is derived from vitamin A absorbs light very strongly in the blue-green region of the spectrum. When it absorbs light, it undergoes a cis-trans isomerization, which induces a conformational change in the protein. This conformational change excites a nerve cell, producing a visual impulse. The compound contains the groups shown in the following table:

Group	Quantity	H group value (kcal/mol)	H contribution (kcal/mol)	S group value (cal/(mol K))	S contribution (cal/(mol K))
C-(H) ₃ (C)	2	-10.20	-20.40	30.41	60.82
C-(C) ₃ (CD)	1	1.68	1.68	-34.72	-34.72
C-(H) ₂ (C) ₂	2	-4.93	-9.86	9.42	18.84
C-(H) ₂ (C)(CD)	1	-4.76	-4.76	9.80	9.80
CD-(C) ₂	1	10.34	10.34	-12.70	-12.70
CD-(C)(CD)	3	8.88	26.64	-14.60	-43.80
CD-(H)(CD)	6	6.78	40.68	6.38	38.28
C-(H) ₃ (CD)	3	-10.20	-30.60	30.41	91.23
C-(H ₂)(CD)(O)	1	-6.76	-6.76	9.80	9.80
O-(C)(H)	1	-37.90	-37.90	29.07	29.07
CY-C6/E	1	1.10	1.10	21.21	21.21
		Total	-29.84		187.83

The NIST group additivity calculator gives the following results:

Quantity	Value
$\Delta_f H^\circ_{\text{gas,est}}$ (kcal/mol)	-27.2
$S^\circ_{\text{gas,est}}$ (cal/mol*K)	178.84

Once again, these differ slightly from the results we obtained by hand, due to some small corrections made by the NIST calculator, but ignored in the manual method. I did not find experimental data for comparison.

(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 Å, estimate the diffusion coefficient of I atoms in this solvent at 298 K.

For a diffusion limited reactant between neutral molecules (or atoms) the rate constant is $k_D = 4\pi r_{AB} D_{AB}$, so $D_{AB} = k_D / (4\pi r_{AB}) = 1.3 \times 10^{10} / (4\pi \cdot 2.2 \times 10^{-10})$ liter mole⁻¹ s⁻¹ m⁻¹ * 1000 cm³/liter * .01 m/cm / (6.022 × 10²³ molecules/mole) = 7.8×10^{-5} cm² s⁻¹. D_{AB} is the diffusion coefficient for A relative to B, so in general, $D_{AB} = D_A + D_B$, where D_A is the diffusion coefficient of species A in the solvent, and D_B is the diffusion coefficient of B in the solvent. So, we should divide D_{AB} by 2 to get the diffusion coefficient of I atoms ($D_I = D_{AB}/2$). However, in the derivation of the diffusion limited rate constant, we assumed that A and B were different. If they are identical, then this results in double counting, just as it did when we were looking at gas phase collisions. So, we must divide the rate by 2, to get $k_D = 4\pi r_{AB} D_{AB}/2$, or $D_{AB}/2 = k_D / (4\pi r_{AB}) = 7.8 \times 10^{-5}$ cm² s⁻¹. So, finally, the factors of two cancel, and $D_I = 7.8 \times 10^{-5}$ cm² s⁻¹.

(b) The temperature dependence of diffusion coefficients in liquids is roughly given by $D = D_o \left(\frac{T}{\mu} \right)$ where μ is the (temperature dependent) viscosity of the solvent.

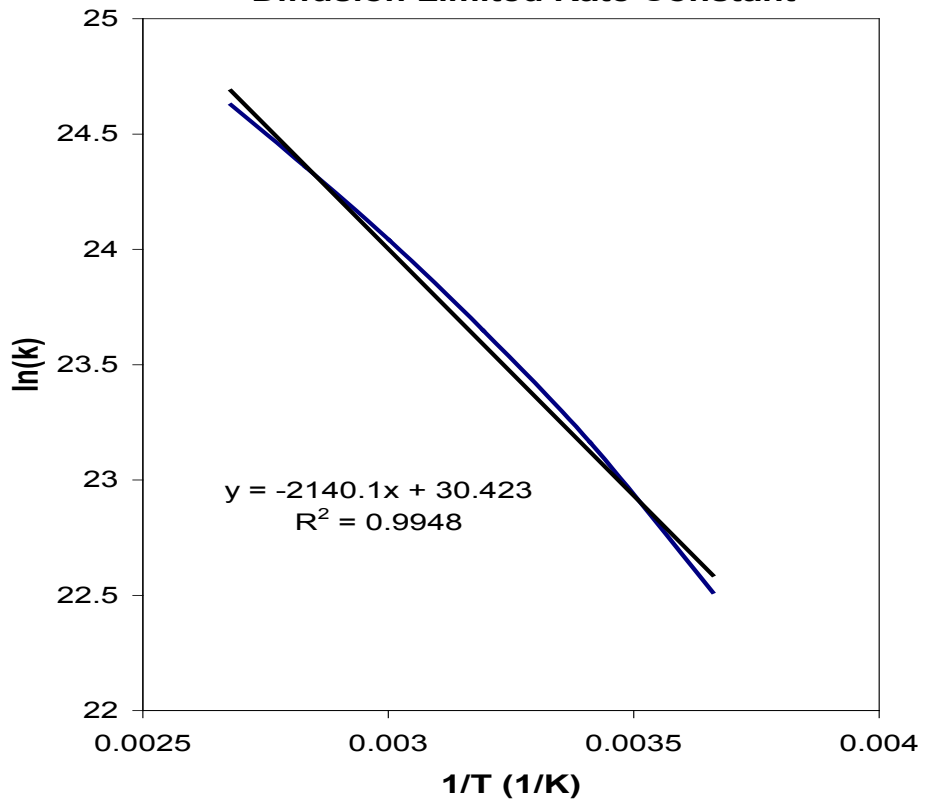
The viscosity of the solvent vs. temperature is

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 I + I reaction for temperatures from 273 to 373 K. What is the apparent activation energy for this diffusion controlled reaction?

The rate constant is just proportional to the diffusion coefficient, which is proportional to T/μ . So, to get the rate constant as a function of temperature, we simply plot $C \cdot T/\mu$ vs. T and vary the constant of proportionality (C) to make it match the value given at 298 K. This gives k_D (liter mol⁻¹ s⁻¹) = $1.3 \times 10^7 (T/\mu)$ with T in K and μ in cP. Making an Arrhenius plot (using the five temperatures and viscosities given) gives an activation energy of 4.25 kcal/mol and a pre-exponential factor of 1.63×10^{13} liter mol⁻¹ s⁻¹. The plot, along with the fit, is shown below.

Diffusion Limited Rate Constant



- (2) 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).***

The total diffusion coefficient at 298 K is $5.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The viscosity at that temperature (interpolating from the data given in problem (1)) is about 0.293 cP. Based on that, the temperature dependent diffusion coefficient can be written as

$$D_{AB} = D_o \frac{T}{\mu} = 4.88 \times 10^{-8} \frac{T}{\mu}, \text{ with } D_{AB} \text{ in } \text{cm}^2 \text{ s}^{-1}, T \text{ in K, and } \mu \text{ in cP.}$$

This gives the temperature dependence of the diffusion-limited rate constant, k_D , which can be computed as

$$k_D = 4\pi D_o \left(\frac{T}{\mu} \right) r_{AB}$$

Everything in this expression is known, except for r_{AB} , which we will determine through the fitting procedure.

The reaction-limited rate constant will be assumed to fit the Arrhenius form

$$k_R = A \exp\left(\frac{E_a}{RT}\right)$$

The parameters A and E_a will also be determined in the fitting procedure. I did this in Excel, with the spreadsheet shown on the next page.

The first two columns have the data, and the next two have the data transformed to be plotted in Arrhenius form. The fifth column has the reaction limited rate constant, calculated using the activation energy and pre-exponential factor at the bottom of the sheet. The sixth column has the viscosity, calculated by fitting the data from problem 2, to the (arbitrary) functional form $\mu = a T^b \exp(c/T)$. The sixth column has the diffusion coefficient, calculated based on that viscosity, and the 7th column has the resulting diffusion-limited rate constant, based on the reaction distance at the bottom of the sheet. The 8th column combines the diffusion-limited and reaction-limited rate constants to give

an effective rate constant. The difference between the log of the fit rate constant (column 10) and the log of the measured rate constant (column 4), was computed, squared, and placed in column 11. The sum of the squared errors, shown at the bottom of the sheet, was minimized by varying r_{AB} , E_a , and A . The values shown gave the best fit. The resulting fit is shown in the plot below the spreadsheet. At high temperatures (left side of the plot) the reaction is diffusion limited, and exhibits a small activation energy. At lower temperatures (right side of the plot) the process is reaction rate limited, and the apparent activation energy is much higher.

T	k_{eff}	1/T	$\ln(k_{eff})$	fit k_R	\square	D_{AB}	fit k_D	fit k_{eff}	$\ln(\text{fit } k_{eff})$	(error) ²
(K)	(liter mole ⁻¹ s ⁻¹)	(K ⁻¹)	(ln(liter mole ⁻¹ s ⁻¹))	(liter mole ⁻¹ s ⁻¹)	(cP)	(cm ² s ⁻¹)	(liter mole ⁻¹ s ⁻¹)	(liter mole ⁻¹ s ⁻¹)	(ln(liter mole ⁻¹ s ⁻¹))	(ln(liter mole ⁻¹ s ⁻¹))
273	8.67E+08	3.66E-03	20.58	9.72E+08	0.582	2.35E-05	7.34E+09	8.58E+08	20.57	9.64E-05
278	1.57E+09	3.60E-03	21.18	1.92E+09	0.499	2.80E-05	8.72E+09	1.57E+09	21.18	1.35E-07
283	2.70E+09	3.53E-03	21.72	3.70E+09	0.431	3.29E-05	1.03E+10	2.72E+09	21.72	4.38E-05
288	4.37E+09	3.47E-03	22.20	6.97E+09	0.376	3.84E-05	1.20E+10	4.41E+09	22.21	7.52E-05
293	6.62E+09	3.41E-03	22.61	1.28E+10	0.331	4.44E-05	1.39E+10	6.67E+09	22.62	4.91E-05
298	9.41E+09	3.36E-03	22.96	2.32E+10	0.293	5.10E-05	1.59E+10	9.43E+09	22.97	8.23E-06
303	1.26E+10	3.30E-03	23.26	4.11E+10	0.262	5.81E-05	1.81E+10	1.26E+10	23.25	4.64E-06
308	1.60E+10	3.25E-03	23.50	7.15E+10	0.235	6.57E-05	2.05E+10	1.59E+10	23.49	4.50E-05
313	1.95E+10	3.19E-03	23.70	1.22E+11	0.213	7.37E-05	2.30E+10	1.93E+10	23.69	9.96E-05
318	2.31E+10	3.14E-03	23.86	2.05E+11	0.194	8.23E-05	2.57E+10	2.28E+10	23.85	1.37E-04
323	2.66E+10	3.10E-03	24.00	3.39E+11	0.178	9.12E-05	2.84E+10	2.62E+10	23.99	1.43E-04
328	3.00E+10	3.05E-03	24.12	5.52E+11	0.164	1.01E-04	3.14E+10	2.97E+10	24.11	1.22E-04
333	3.34E+10	3.00E-03	24.23	8.85E+11	0.151	1.10E-04	3.44E+10	3.31E+10	24.22	8.48E-05
338	3.68E+10	2.96E-03	24.33	1.40E+12	0.141	1.20E-04	3.75E+10	3.66E+10	24.32	4.49E-05
343	4.02E+10	2.92E-03	24.42	2.19E+12	0.132	1.31E-04	4.07E+10	4.00E+10	24.41	1.40E-05
348	4.35E+10	2.87E-03	24.50	3.37E+12	0.124	1.41E-04	4.40E+10	4.35E+10	24.50	2.21E-07
353	4.68E+10	2.83E-03	24.57	5.13E+12	0.117	1.52E-04	4.74E+10	4.69E+10	24.57	8.91E-06
358	5.01E+10	2.79E-03	24.64	7.72E+12	0.110	1.63E-04	5.08E+10	5.04E+10	24.64	4.29E-05
363	5.34E+10	2.75E-03	24.70	1.15E+13	0.105	1.74E-04	5.42E+10	5.39E+10	24.71	1.03E-04
368	5.66E+10	2.72E-03	24.76	1.69E+13	0.100	1.85E-04	5.76E+10	5.74E+10	24.77	1.90E-04
373	5.98E+10	2.68E-03	24.81	2.46E+13	0.096	1.96E-04	6.10E+10	6.08E+10	24.83	3.02E-04
		D_0		r_{AB} (Å)		E_a (kcal/mole)	$\ln(A)$ (ln(liter mole ⁻¹ s ⁻¹))			Sum(error ²)
		5.02E-08		4.120		20.52		58.52		1.62E-03

Homework 7, Problem 3

