Chemistry 4000/5000/7000 Fall 2021
Final Examination

Due: No later than 8:00 p.m. on December 15th

Please submit your answers electronically. Neatly handwritten work is acceptable. If you need to submit additional files (e.g. submission of a spreadsheet is encouraged in one question), send everything as one email with multiple attachments.

Total marks: 66

No collaboration is permitted between students for this exam. You are not to discuss the questions or their solutions with classmates or with anyone else before the deadline for returning papers. Attempting to get help via an online forum is expressly forbidden.

I may answer questions at my discretion if you require clarifications. Don't hesitate to ask. I will generally propagate any answers offered to one student to the entire class via email.

Detailed solutions or answers are required. Little to no credit will be given for answers presented without your detailed reasoning. However, do look at the number of marks assigned to a question. As a rough rule of thumb, a 10-mark question might require about a page of math, or three to five substantial paragraphs.

For computational problems, you must provide sufficient detail of the calculation to enable replication by an expert user of the software. **Don't** submit input or output files. You will be graded partly on your ability to clearly communicate important details.

Note: Some computations may be time-consuming. Don't wait until the last minute to carry out computations!

Fundamental constants: Please use these values.

$$\begin{aligned}
c &= 2.997\,924\,58 \times 10^{8}\,\mathrm{m\,s^{-1}} \\
h &= 6.626\,070\,015 \times 10^{-34}\,\mathrm{J\,Hz^{-1}} \\
k_B &= 1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}} \\
L &= 6.022\,140\,76 \times 10^{23}\,\mathrm{mol^{-1}} \\
R &= 8.314\,462\,618\,\mathrm{J\,K^{-1}mol^{-1}}
\end{aligned}$$

Good luck!

1. Potential energy surfaces and their features have been a recurring theme in this course. Discuss the various ways in which we made use of potential energy surfaces either conceptually or computationally. In each case, what part(s) of the potential energy surface is important? **15 marks**

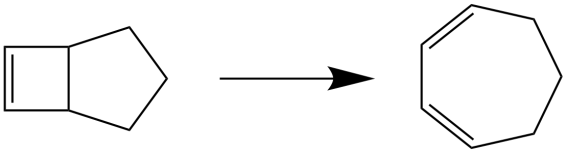
2. In this question, you will compare the collision/diffusion-limited rate constants in the gas phase and in solution. Suppose that we have a bimolecular reaction A + B → products. Assume the two reactants are uncharged hard spheres with the following properties: **12 marks**

	r/Å	M/g mol^{-1}
A	3.8	150
B	5.0	332

Assume the reaction is collision-limited in the gas phase and diffusion-controlled in solution. Predict the rate constants in the gas phase and in ethylene glycol solution for this reaction at 100 °C. At this temperature, the viscosity of ethylene glycol is 1.975 mPa s. In which medium (gas or solution) is the reaction fastest? Is the difference large? Is this what you would have expected?

Note: There are no 'right' or 'wrong' answers to the qualitative questions. I'm just curious what you think.

3. In class, we analyzed the data of Branton and coworkers[1] for the reaction **20 marks**



   (a) This reaction was studied in the gas phase over the temperature range 274.5 to 327.1 °C, and in dimethyl phthalate solution over the temperature range 256.2 to 288.4 °C. The reaction has the following Arrhenius parameters:

	$E_a/\mathrm{kJ\,mol^{-1}}$	$A/10^{14}\mathrm{s}^{-1}$
Gas	191.1 ± 0.6	2.28 ± 0.30
Solution	191.3 ± 2.0	4.0 ± 1.8

   Calculate $\Delta^{\ddagger}\Delta_{\mathrm{solv}}G^{\circ}$ for this reaction. Explain the meaning of the sign of the result. If possible, put the size of the result in perspective. [6 marks]

   Be sure to briefly explain the basis for any decisions you make as you are working on this problem.

   (b) The experiments in solution gave the following rate constants:

$T/^{\circ}\mathrm{C}$	256.2	259.9	265.2	268.5	273.8	280.4	283.5	288.4
$k/10^{-4}\,\mathrm{s}^{-1}$	0.513	0.705	1.11	1.43	2.18	3.37	4.39	6.40

   Determine the enthalpy and entropy of activation for this reaction. [10 marks]

   Notes: We haven't done this type of problem in this course, but the textbook explains what you need to do. It may be a good idea to use a spreadsheet for this problem. If you do, instead of writing up a solution by hand, I would encourage you to submit your spreadsheet. Using a spreadsheet does not absolve you from clear labeling of your work or from showing units. This includes axis labels on graphs. Given that it is tricky to make labels and units look nice in a spreadsheet, I will be lenient about notation provided it's clear.

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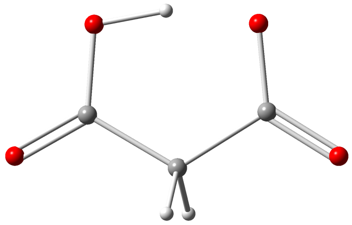
[1] Branton et al., *Trans. Faraday Soc.* **62**, 659 (1966)

(c) Transition-state theory suggests that, instead of a potential energy barrier to reaction, we should think in terms of a free energy barrier. Based on your calculations, for this reaction in solution, which is the more important contributor to the free energy barrier, the enthalpic or entropic contribution? Can you generate a plausible hypothesis why this might be? [4 marks]

Again here I'm not necessarily looking for a specific answer to the 'why' question. I want to see if you can generate a logical argument based on your knowledge of general physical chemistry.

4. The hydrogen malonate anion $HOOCCH_2COO^-$ has the following equilibrium structure: **19 marks**



This exam is being distributed with a Gaussian input file that contains the coordinates of this ion in a computed equilibrium geometry.

(a) Calculate the rate constant for transfer of the acidic proton from one oxygen to the other in the gas phase at 25 °C and 1 bar using transition-state theory. Make sure to discuss your choice of computational methods. Note that the method embedded in the Gaussian input file distributed with this assignment may or may not be the best method to use for many reasons, including the amount of time you have available to devote to this computation. [10 marks]

(b) I specified the pressure in part (a). Does it matter? Why or why not? [2 marks]

(c) If you had lots of time, would you try to calculate a tunneling correction for this reaction? Why or why not? [2 marks]

(d) If you wanted to calculate the rate constant for this reaction in aqueous solution, what would you need to do and why? What complications might make it difficult to calculate an accurate rate constant? [5 marks]

Bonus: During the derivation of the RRK equation, we calculated $\ln p^{\ddagger}$. Show that this term can be interpreted as the change in entropy during IVR. [4 marks]