

Chemistry 271 – 23XX

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General Chemistry and Energetics

Exam I (100 points)

Your Name: Keg

Your SID #: _____

Your Section # or time: _____

October 2, 2018

You have 53 minutes for this exam.

Explanations should be concise and clear. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pH = -\log([H^+])$$

$$(P-nb)(P+an^2/V^2) = nRT$$

$$R = 0.08206 \text{ L}\cdot\text{atm/mole K}$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$\ln K_{eq} = -\Delta H^\circ/(RT) + \Delta S^\circ/R$$

$$R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_A k_B$$

$$\ln k = \ln A - E_a/(RT)$$

$$^\circ\text{C} = ^\circ\text{K} - 273.15$$

$$P(v)dv = Cv^2 \exp(-mv^2/2kT)$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_p = K_c(RT)^{\Delta n}$$

$$\text{Mass of H: } 1.008 \text{ g/mole}$$

$$E = mc^2$$

Integrated rate laws for 0, 1, 2 order:

$$[A] = [A]_0 - kt$$

$$\ln[A] = \ln[A]_0 - kt$$

$$1/[A] = 1/[A]_0 + kt$$

$$t_{1/2} = [A]_0/(2k)$$

$$t_{1/2} = \ln 2/k$$

$$t_{1/2} = 1/(k[A]_0)$$

$$N = R_* \cdot f_p \cdot n_e \cdot f_\ell \cdot f_i \cdot f_c \cdot L \quad PV = nRT$$

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

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1. Chemical Equilibrium (30 pts)

Fill in the blanks or circle the correct answers below. Consider the reaction $A + 2B \xrightleftharpoons[k_{-1}]{k_1} C + D$ and assume (probably incorrectly) that the forward and reverse reactions are both elementary.

(a; 6 pts) If the reaction is at equilibrium, the rates / rate constants for the forward and reverse reactions are equal to each other / equal to zero. The concentrations of A, C, and D are equal to each other / constant with time. (+2) each

(b; 4 pts) Whether or not the reaction has reached equilibrium, the differential rate law for the rate of change of [C] is given by:

$$\frac{d[C]}{dt} = -k_{-1}[C][D] + k_1[A][B]^2$$

+2 for any answer that would be a rate law
+2 for correct

(c; 4 pts) Show that setting the rate of change of [C] = 0 and rearranging gives us the familiar expression for the equilibrium constant K.

$$\begin{aligned} -k_{-1}[C][D] + k_1[A][B]^2 &= 0 \\ k_1[A][B]^2 &= k_{-1}[C][D] \\ \frac{k_1}{k_{-1}} &= \frac{[C][D]}{[A][B]^2} = K \checkmark \end{aligned} \quad \left. \begin{array}{l} (+2) \text{ for any setup} \\ (+2) \text{ for getting to } K \end{array} \right\}$$

(d; 5 pts) Does setting $d[C]/dt = 0$ above mean that we have invoked the Steady State Approximation for [C]?
Yes / No. Explain your reasoning very briefly.

No (+2)
+3 for correct or clear good answer
this is dynamic equilibrium, not the rapid response of an intermediate - [C] is a stable species - there is no apparent rapid decay path.

(e; 6 pts) If the equilibrium concentrations of A, B, C, and D are 1.5 mM, 2.0 mM, 1.7 mM, and 3.0 mM

respectively (1 mM = 0.001 M), the numerical value of K is 850. We know that K is unitless, but if we wanted to specify units for the purpose of disambiguation the units would be M⁻¹.

$$K = \frac{(1.7)(3.0) \times 10^{-6}}{(1.5)(2.0)^2 \times 10^{-9}} = 0.85 \times 10^3 = 850 \quad (+2) \quad (+2) \quad (+1)$$

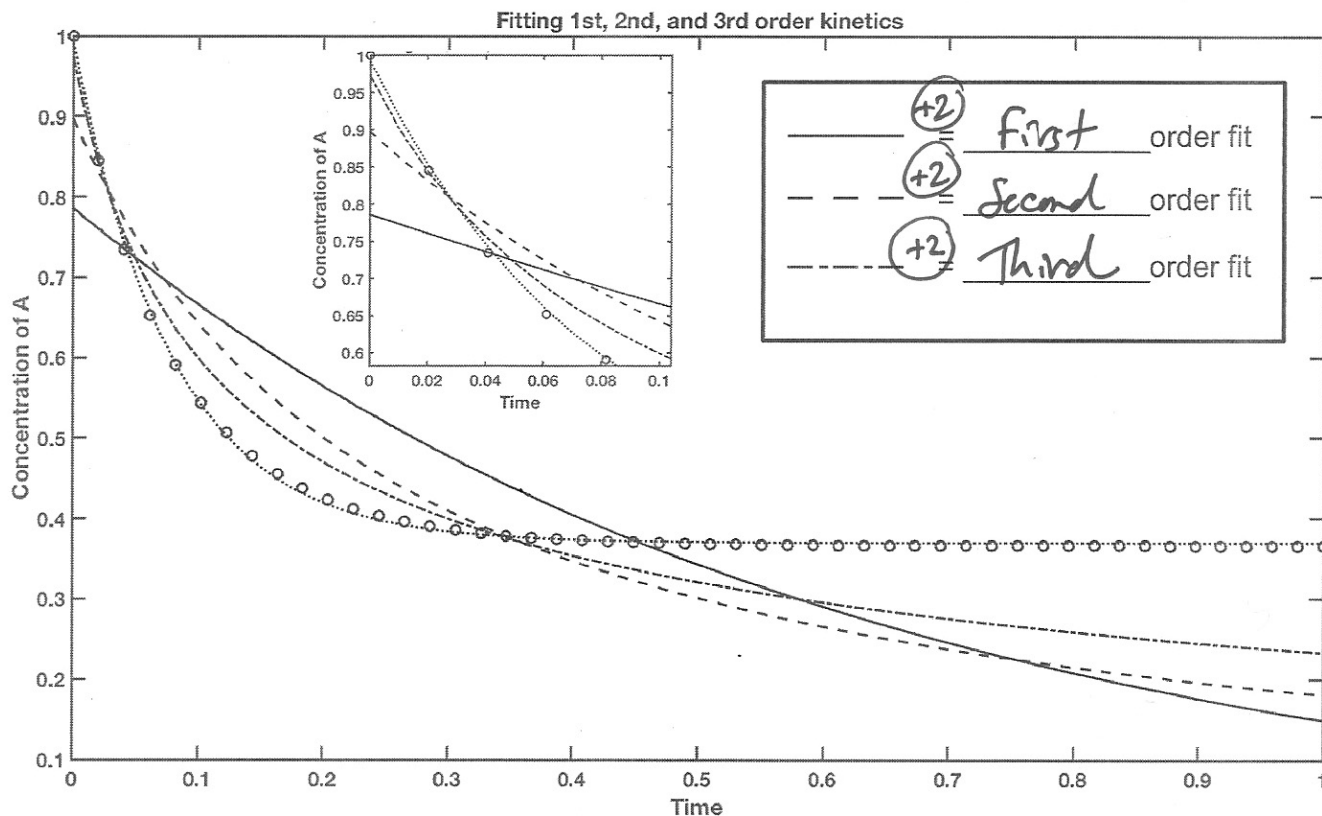
(f; 5 pts) Given the above, if the rate constant $k_{-1} = 8.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, the rate constant $k_1 = \underline{7.2 \times 10^8 \text{ M}^{-2}\text{s}^{-1}}$

OK if consistent w/ e (+2)

$$850 = \frac{k_1}{k_{-1}} \quad k_1 = 850 \text{ M}^{-1} \times 8.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1} = 7.2(25) \times 10^8 \text{ M}^{-2}\text{s}^{-1}$$

2. Chemical Kinetics (30 pts)

Note: you can answer some parts of this question independently but it might help to read the whole question first. You and your lab mates measure a time course for the reaction $A \rightarrow C$, using the decrease in the absorbance at 350 nm, in the UV. "A" is the only absorbing species. You convert the absorbance data to concentration, and you obtain the results shown as the circles in the plot below.



(a; 3 pts) Naturally, the first order of business, as it were, is to determine the order of reaction. Your lab mate decides to fit the data to 1st, 2nd, and 3rd order integrated rate laws using non-linear least squares analysis. How could they tell from just looking at the data that there was no point fitting the zero-order rate law?

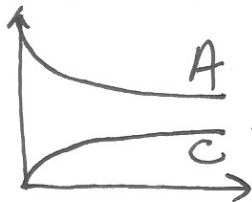
Zero order reactions have $[A] = [A]_0 - kt$ so linear - this clearly isn't that. (+3)

(b; 10 pts) Your lab mate plotted the solid line, the dashed line, and the dot-dashed line. However, they omitted to label which is first order, second order, and third order. Indicate which is which in the box on the plot above, and give your reasoning below. (We did not study the third order rate law but you should be able to guess what it looks like. Hint: think about how the slope of the $[A]$ vs. t curve changes with time as reactant is depleted for zero vs. first vs. second order rate laws.)

- As the reactant order increases, the rate decreases more rapidly as the reaction progresses, so the curve gets progressively steeper at the beginning and flatter at the end. (+3)

points add to 12 - 10 is max allowed

(c; 8 pts) Clearly, none of these curves fit very well. Assuming that you started with pure A and that it converts only to pure C and that C does not have any absorbance, give a likely explanation for the shape of the observed curve, and explain why the fits that assume simple integrated rate laws did not work. Suggest an experiment to test your theory. Hint: we have interpreted curves in lecture that look just like this.



ATC must be constant - this looks very similar to the plot illustrating dynamic equilibrium for $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.

Here $A \rightleftharpoons C$ so the concentration of $[A] \neq 0$.

- Simple fits don't work b/c they assume an irreversible reaction - $[A]$ should always go to 0 eventually.
- Start with $[C]$ and see if we get $[A]$?

(d; 4 pts) Problems with deriving rate laws from time courses like this happen in real life, or at least lab life, all the time. Explain very briefly why we use initial rate measurements to get around them.

Initial rates are unaffected by accumulation of product so they can be measured without worrying about whether the reaction reaches equilibrium, whether inhibitors develop during the reaction, or whether possible catalysts are inhibited by product. [Of course, \therefore you miss a lot!]

+2 for any reason

(e; 5 pts) Then, just as you were ready to turn in your lab report, your other lab partner shame-facedly admits that they had placed entirely the wrong sample in the cuvette. You were not studying A at all! You had a mixture of unknown amounts of D and E in the cuvette and you were looking at the irreversible reaction $D + E \rightarrow F$. D absorbs at 350 nm (thereby mimicking A so you didn't catch the problem in the moment) but neither of the other molecules do. Propose a new explanation for the shape of the absorbance vs. time curve.

$D + E \rightarrow F$ should be second order, but if E is present at lower concentration than D, then $D + E \rightarrow F$ proceeds only until E is used up at which time $[D]$ remains constant, looking much like the data shown.

[Not exactly like the data b/c in principle a 2nd order reaction never quite goes to completion]

Play with ABCDEF kin 2 to explore.

3. Miscellaneous kinetics (40 pts)

(a; 15 pts) A rule of thumb in organic chemistry states that for many reactions the rate of reaction doubles for every 10 °C (or K) increase in temperature, for temperatures near 300 K. This is an approximation: assuming the reaction follows the Arrhenius rate law, what value of E_a makes it exactly true, going from 330 to 340 K?

We assume that for a given reaction we have $k = Ae^{-E_a/RT}$ where A is a constant independent of T . (+2) OK if implicit Kelvin...not Key (+2)

We are told that $k(340\text{ K}) = 2 \cdot k(330\text{ K})$ (+2) [here $k(T)$ is k as a function of T]

Then $Ae^{-E_a/R \cdot 340\text{ K}} = 2 \times Ae^{-E_a/R \cdot 330\text{ K}}$ (+3)

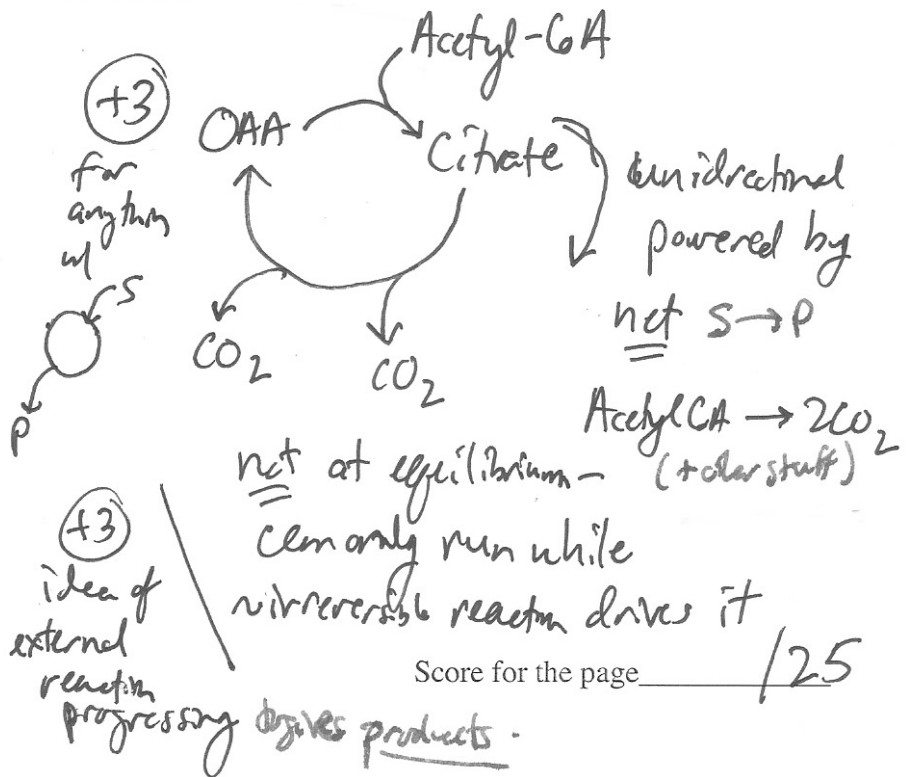
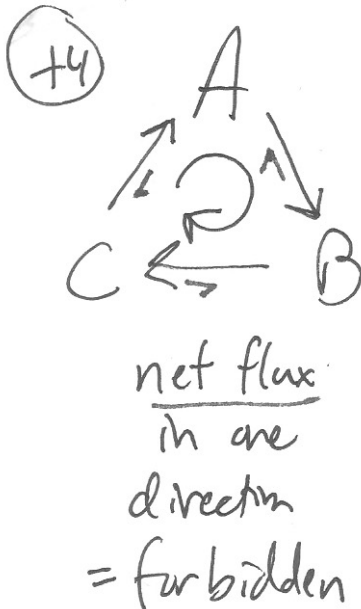
Logs: $-\frac{E_a}{R \cdot 340\text{ K}} = \ln 2 - \frac{E_a}{R \cdot 330\text{ K}}$

$\frac{E_a}{R} \left(\frac{1}{330\text{ K}} - \frac{1}{340\text{ K}} \right) = \ln 2$

(+3) for math [Very ~ to an assigned HW problem] (+3) 64.6 kJ/mol

$E_a = \left(\frac{1}{330\text{ K}} - \frac{1}{340\text{ K}} \right)^{-1} \cdot \ln 2 \cdot 8.314 \text{ J/mol K} = \underline{64.6 \text{ kJ/mol}}$ (+3) ~~64.6 kJ/mol~~ \rightarrow + sign instead of -

(b; 10 pts) The law of microscopic reversibility and the conservation of energy forbid cyclic reactions in isolation. Sketch what we mean by a forbidden cycle. On the other hand, biochemistry is full of cycles, like the Krebs cycle in intermediary metabolism, which adds acetyl-CoA to OAA to make citrate and then converts citrate back into OAA through a series of reactions that occasionally spit out CO_2 . Draw a second sketch to explain how biology can get away with a cyclic reaction.



Score for the page 25

(c; 10 pts) The integrated rate law for a first order reaction is $[A] = [A]_0 e^{-kt}$. Use the definition of the half-life to derive the equation for the half-life in terms of k . Explain why the half-life is a much more useful concept for first-order processes than it is for zero-order or second-order processes.

At ~~t~~ $t = t_{1/2}$, $[A] = \frac{1}{2} [A]_0$ - def'n of half-life
(+2) (implicit OK)

$$\frac{1}{2} [A]_0 = [A]_0 e^{-kt_{1/2}}$$

$$-\ln 2 = -kt_{1/2} \quad \left. \begin{array}{l} (+3) \\ \text{for some} \\ \text{math} \end{array} \right\}$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (+2)$$

$t_{1/2}$ is independent of concentration for 1st order so it doesn't depend on initial concentration and it remains constant throughout the rxn.
(+3)

(d; 5 pts) Use the ideal gas law to show that the pressure of a gas in a sealed vessel is directly proportional to temperature.

$$PV = nRT \quad \left(\begin{array}{l} (+1) \\ \text{cancel} \end{array} \right)$$

$$P = \left(\frac{nR}{V} \right) T \quad (+2) \quad \frac{P}{T} = \frac{nR}{V}$$

constant for a sealed vessel
(+2)

Page	Score
2	/30
3	/13
4	/17
5	/25
6	/15
Total	/100

Score for the page 15