Chemistry 271 – 23XX

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General Chemistry and Energetics

Exam I (100 points)

Your Name: _Key_

Your SID #: _____

Your Section # or time: _____

February 29, 2016

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:

$K_a = [H^+][A^-]/[HA]$ $pH = -\log([H^+])$ $K_b = [HA][HO^-]/[A^-]$

$R = 0.08206 \text{ L·atm/mole K}$ $k_B = 1.38 \times 10^{-23} \text{ J/K}$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

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

$°C = °K - 273.15$ $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\ln k = (-E_a/RT) + \ln A$

Integrated rate laws for 0, 1, 2 order:

$[A] = [A]_0 - kt$ $\ln[A] = \ln[A]_0 - kt$ $1/[A] = 1/[A]_0 + 2kt$

$t_{1/2} = [A]_0/(2k)$ $t_{1/2} = \ln2/k$ $t_{1/2} = 1/(2k[A]_0)$

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."

1. Explanations (21 pts)

(a; 9 pts) Briefly and generally describe the overall flow for using kinetic measurements to evaluate a proposed mechanism for a chemical reaction.

(+2) — Measure [ ]'s vs. time for the reaction of interest

(+3) — Extract the rate law from the experiment by plotting the data in one of the linear forms, fitting the kinetic equations to the data using non-linear least-squares, or a log/log plot

(+2) — Use the proposed mechanism to predict the integrated rate law, the differential rate law, or for numerical integration

(+2) — Compare prediction to experimental rate law — if they agree, the mechanism is possible, if they don't it is wrong.

→ +5 for just extracting rxn order + k w/ no connection back to mechanism

(b; 12 pts) Explain how the Maxwell-Boltzmann distribution of gas speeds leads to the Arrhenius equation for the temperature dependence of the rate constant. Sketch an Arrhenius plot with the axes, slope, and intercept labeled.

(+2) — The Maxwell-Boltzmann distribution says that at large energies, the likelihood of a particle having a given energy is an exponentially decreasing function of the energy.

(+2) — The Arrhenius rate law postulates that some minimum energy is needed to make a reaction occur, so the probability of having that energy is an exponentially decreasing function of energy as in the M-B.

— This gives $k = A e^{-E_a/RT}$

(+2) — where RT is proportional to the average energy per particle

(+2) idea

$slope = -E_a/R$
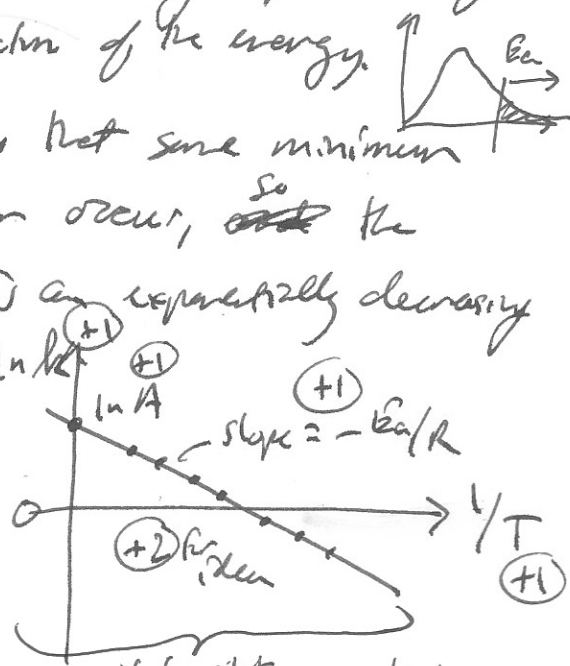
+6 for plot

Score for the page _____ /21

— Many students did not know what an Arrhenius plot is.

2. Ideal Gas Law (20 pts)

(a; 10 pts) A standard Size 300 gas cylinder has an internal volume of 49 L. In such a cylinder filled with nitrogen, treating the N_2 as an ideal gas, how many moles of N_2 are there and how much does the N_2 (MW 28) weigh, at a partial pressure of N_2 of 180 atm, at 21 °C?

(+1) $PV = nRT$

(+3) $180 \text{ atm} \cdot 49 \text{ L} = n \cdot 0.08206 \text{ L atm/mole K} \cdot (273.15 + 21) \text{ K}$

(+3) $n = \dfrac{180 \cdot 49 \text{ moles}}{0.08206 \cdot 294.15} = 365.40 \text{ moles}$ or 3.6×10^2 moles

(sig figs ~~false~~ are not graded)

(+3) $365.40 \text{ moles} \cdot 28 \text{ g/mole} = 10231 \text{ g}$ or 10. kg

(b; 3 pts) What volume would the contents of the cylinder occupy at 1 atm pressure?

$P_1 V_1 = P_2 V_2$ $V_2 = \dfrac{P_1 V_1}{P_2} = \dfrac{180 \cdot 49}{1} = 8820 \text{ L or } 8.8 \text{ m}^3$

(+2)   (+1)

(c; 2 pts) If one had the same cylinder filled with Argon (MW 40) at the same pressure and temperature, how many moles of Ar would it contain?

(+2) It's an ideal gas — P depends only on n, T, P so n = 365

A lot of people losing points by not stating this.

(d; 5 pts) Would the Ar atoms move on average faster or slower than the N_2 molecules, and why?

(+2)

(+1) Slower — At constant T, kinetic energy per particle is the same, so since Ar has greater mass, it will have smaller velocity for constant $\frac{1}{2}mv^2$.

(+2)

Score for the page _____ 20

3. Kinetics (30 pts)

(a; 12 pts) The radioactive isotope ^{32}P has a half-life of 14.3 days, decaying into $^{32}S + e^-$. The half-life is independent of the amount of ^{32}P. Write down the rate law for the decay process, and calculate the rate constant. What fraction of the initial sample remains after 6 months (182 days)?

If $t_{1/2}$ is independent of [ ], process must be first order

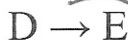(+3) so $-\dfrac{d[^{32}P]}{dt} = k[^{32}P]$ or $[^{32}P] = [^{32}P]_0 e^{-kt}$

(+3) $t_{1/2} = \ln 2/k$ so $k = 0.693/t_{1/2} = 0.0485 \text{ days}^{-1}$ either is fine

$= 5.61 \times 10^{-7} \text{ s}^{-1}$

only +1 if no units

$\dfrac{[^{32}P]}{[^{32}P]_0} = e^{-kt} = e^{-(0.0485 \text{ days}^{-1})(182 \text{ days})} = 1.47 \times 10^{-4}$
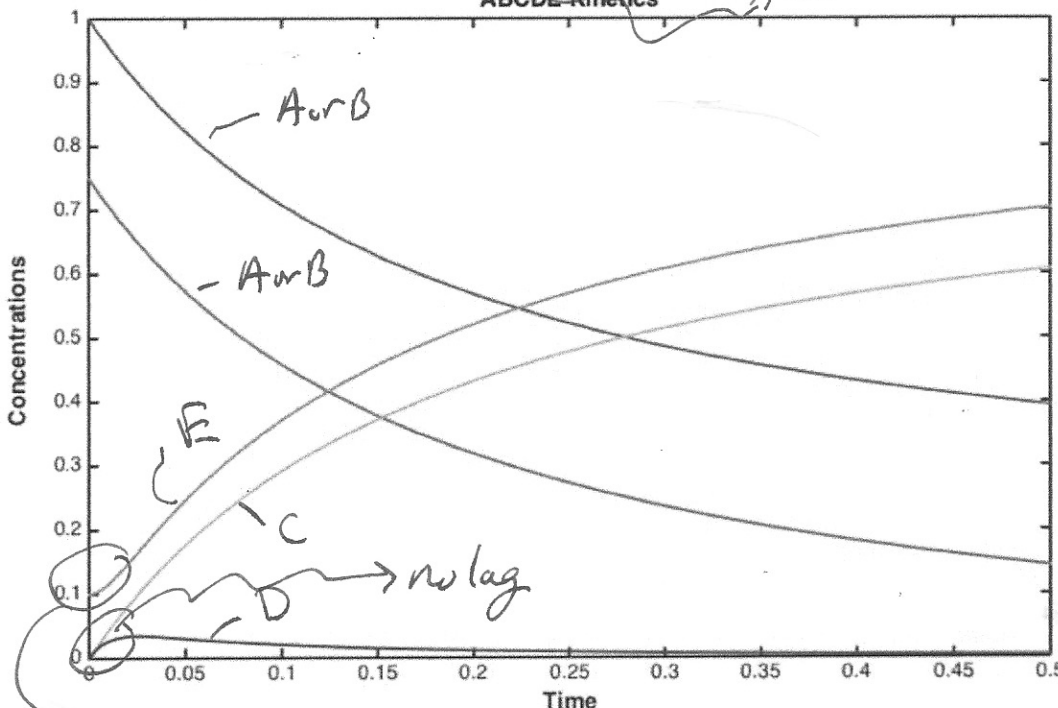
(+3)

(+3) or 12.73 halflives

+1 for some # like $\left(\frac{1}{2}\right)^{12.73}$

The graph below shows kinetics for the reaction scheme below, where the reactions shown are elementary. We start with mostly A and B, with a smaller amount of C or E also present.

$$A + B \rightleftharpoons C + D$$
$$D \rightarrow E \quad k_1$$
$$\rightarrow k_2$$

ABCDE Kinetics

note lag — initially lower slope

Score for the page ___/12

(b; 5 pts) Label the five kinetic traces as (A or B), (A or B), C, D, and E. (There is no way to distinguish A and B from the information given.)

(+1) point each

(c; 4 pts) Explain how you identified the curve that starts at Concentration = 0.1 as either C or E; it is subtle.

(+2) There is a slight lag. (+1) A+B produces C with no lag time, but production of E depends on formation (+1) and breakdown of D, so there is a lag. Also ~ rate of C+D formation is the same.

6

(d; 7 pts) The curve for D represents a steady state intermediate. Write down the differential rate equation for the concentration of intermediate D. What does the SSA tell us about the numerical value of d[D]/dt?

$$\frac{d[D]}{dt} = k_1[A][B] - k_{-1}[C][D] - k_2[D] = 0$$

(+1)   (+1)   (+1)   (+1)

SSA (+3)

(+2)
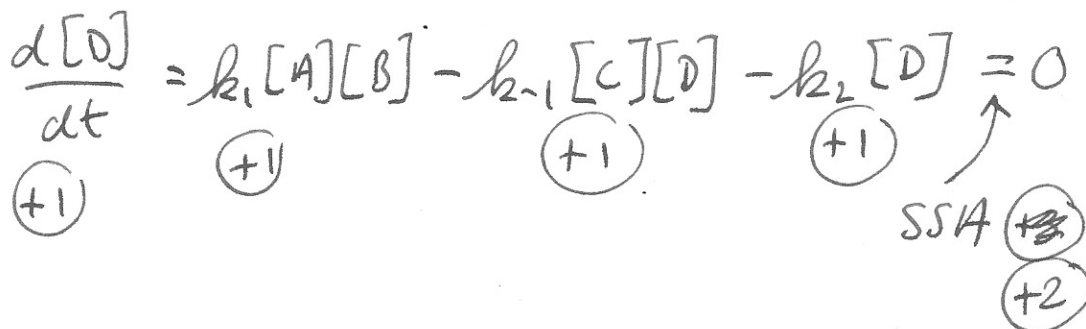
3

(e; 2 pts) Has the reaction reached equilibrium at t = 0.5? Circle one: Yes (No) (+1). Explain how you know.

The lines are still changing (+2)

Score for the page _____ /18

4. LeChatelier's Principle (29 pts)

The equilibrium below is called the Water-Gas Shift Reaction (WGSR). It is important in industrial hydrogen production. The WGSR is performed at high enough temperature that all of the components are gases at all times, and we assume that all the gases behave as ideal gases.

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$
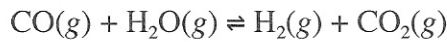
Consider a mixture of CO and water that has been allowed to come to equilibrium, under conditions chosen so that at equilibrium there are substantial partial pressures of all four gases.

(a; 2 pts) What do we know about the overall rates of the forward and reverse reactions at equilibrium?

(+2) They are equal

Now, additional pure CO is added to the reaction vessel. LeChatelier's principle tells us about what happens next, qualitatively.

(b; 6 pts) Explain which way the equilibrium shifts, and why, according to LeChatelier.

(+1) — Adding CO is a stress on the equilibrium

(+2) — It will respond to decrease the stress, i.e. decrease the P_{CO}

(+3) — So the equilibrium will shift to the right, consuming CO.

(c; 3 pts) If someone's answer to (b) had something to do with a response to a change in the total pressure of the gas mixture, it was wrong. Why?

Shifting the equilibrium left or right does not change the total pressure.

(d; 6 pts) Now give an explanation for the shift in the equilibrium you described in (b) based on the kinetics of the forward and reverse reactions, as an alternative to LeChatelier's principle.

(+2) — The rate of the forward reaction goes up because there is more reactant. [there are subtleties b/c it is the rxn but

(+2) — The rate of the reverse reaction is unchanged.

(+2) — Therefore there is net flux in the forward direction until the rate of the forward rxn ↓ and the rate of the reverse rxn ↑ until they are equal again.

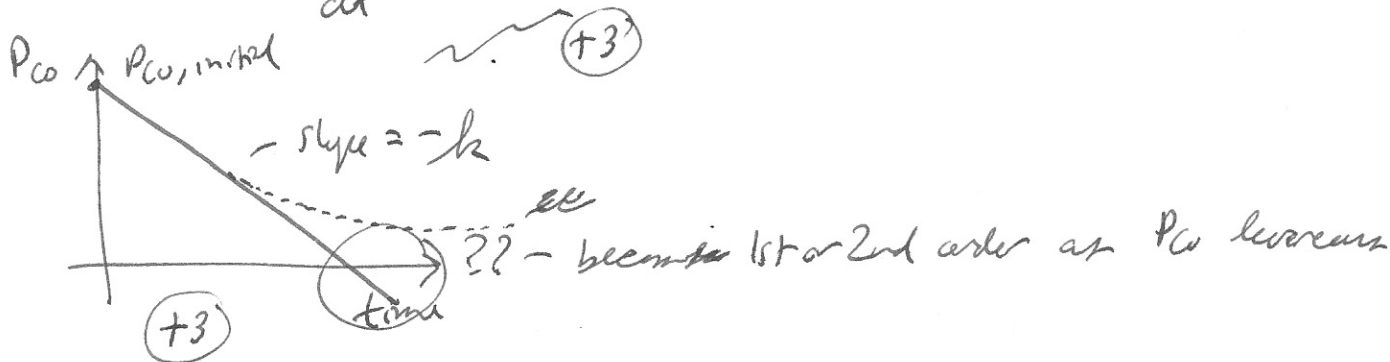demanding — more complex explanations are possible]

Score for the page _____ /17

(e; 2 pts) When the mixture re-equilibrates, the final partial pressure of CO will be (circle one): equal to, (more than), or less than the partial pressure before the addition of CO.

(+2) the stress is not completely relieved (no explanation needed)

6

(f; 7 pts) The WGSR can be catalyzed by a variety of metal complexes, with complicated and irrelevant mechanisms, and the uncatalyzed reaction is slow enough to be ignored. If we start a reaction with large partial pressures of CO and water, no H_2 or CO_2, and a very small amount of catalyst, what rate law would you expect to observe for the kinetics of CO oxidation? Sketch the one form of the graph for the partial pressure of CO (P_{CO}) vs. time (choosing from among P_{CO} vs. time, $\ln(P_{CO})$ vs. time, and $1/P_{CO}$ vs. time) that gives a linear form from which we could extract a rate constant.

High [CO] and [H_2O] - catalyst will always be saturated

$$Rate = -\frac{d\,P_{CO}}{dt} = k \quad or \quad k\,[active\ catalyst] \quad \overset{pseudo-}{zero\ order}$$

(+3)

P_{CO} ↑ $P_{CO,\,initial}$

- slope = -k

?? - becomes 1st or 2nd order as P_{CO} lessens

time

(+3)

4

(g; 3 pts) If we doubled the amount of CO, what would happen to the measured rate constant under these conditions? If we doubled the amount of catalyst, what would happen to the measured rate constant?

(+2) — The rate would stay the same — the catalyst is saturated

(+2) — The measured rate constant would ~~double~~ double (or stay the same if it was given as k [catalyst] above.

Page	Score
2	/21
3	/20
4	/12
5	/18
6	/17
7	/12
Total	/100

Score for the page_____ /12