Chemistry 134
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General Chemistry and Energetics
Exam I (100 points)

Your Name: Key

Your SID #:

Your Section # or time:

March 10, 2017

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:

$K_a = [H^+][A^-]/[HA]$ $\quad$ $pH = -\log([H^+])$ $\quad$ $(V-nb)(P+an^2/V^2) = nRT$

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

$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$ $\quad$ $\ln k = (-E_a/RT) + \ln A$

$°C = °K - 273.15$ $\quad$ $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\quad$ $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$f = \left(\frac{c + v_r}{c + v_s}\right) f_0 \qquad \frac{d}{dx}\int_a^x f(s)\,ds = f(x) \qquad \hat{f}(\xi) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i x \xi}\,dx$$

Integrated rate laws for 0, 1, 2 order:

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

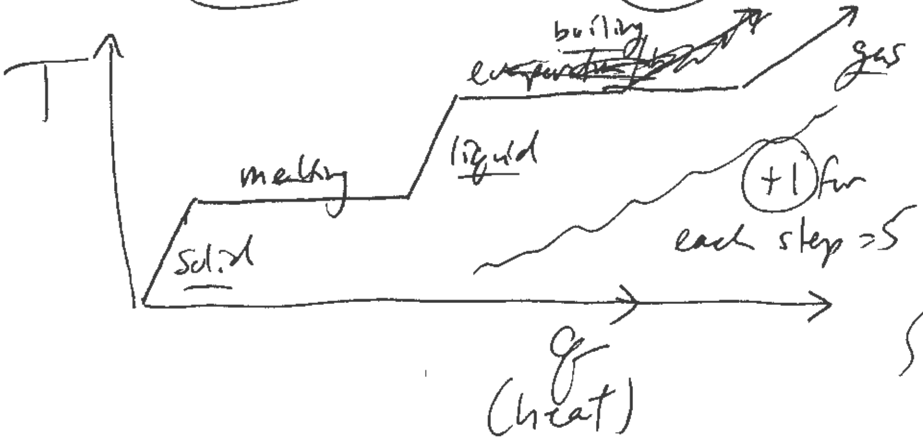
$t_{1/2} = [A]_0/(2k)$ $\quad$ $t_{1/2} = \ln 2/k$ $\quad$ $t_{1/2} = 1/(k[A]_0)$

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. States of Matter (22 pts)

(a; 12 pts) Sketch a heating curve for a typical substance as it converts from solid to liquid to gas at constant pressure. Physically, what is happening in each of the flat parts?



(+1) for each step = 5

} slopes inversely proportional to heat capacity] not needed

(+3) for idea

"phase transition" = +2

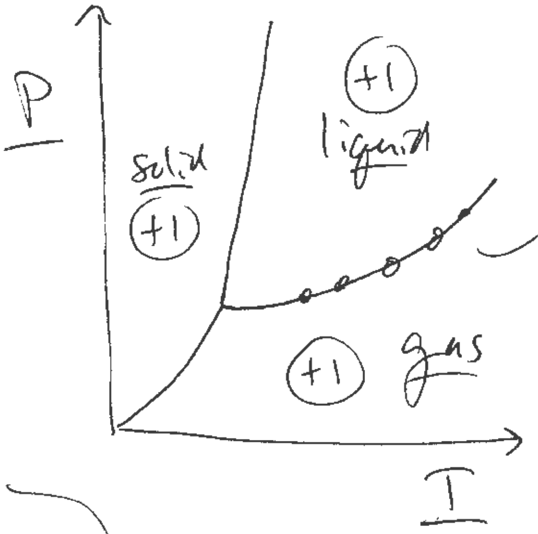
(+2) Melting: progressive conversion of solid → liquid with no change in T.

(+2) Boiling: " " " liquid → gas " " " " ",

both phases present (+2), (+1) each for description

(b; 10 pts) Sketch a P/T phase diagram for a generic pure substance. The Phase Rule says that F = C – P + 2, where F = degrees of freedom, C = # of components, and P = # of phases. Explain what the Rule means in reference to the liquid-gas coexistence curve on your phase diagram.

[illegible]



(+2) for idea

Along the coexistence curve,

(+2) $F = 1 - 2 + 2 = 1$. There is one degree of freedom, meaning that we can choose

(+3) either P, T (or total molar V), but then the others are set by properties of the system. (maintaining coexistence)

Score for the page____________

2. Ideal and Non-ideal Gases (31 pts)

(a; 8 pts) Why do real gases act more and more like the ideal gas (i) as temperature increases and (ii) as density decreases (answer (i) and (ii) individually)?

(+2)

(i) As T ↑, molecules move more rapidly and therefore spend less time in the vicinity of other molecules – the influence of intermolecular forces decreases. (+2) And/or at constant P the volume ↑ so excluded volume is less important. /[+4]

(+2)

(ii) As density (n/v) ↓, the fraction of volume that is excluded decreases. Also there are fewer molecules around exerting attractive forces. (+2)

(b; 10 pts) What is Dalton's law of partial pressures? How does it follow from the assumptions made in deriving the ideal gas equation? Propose an experiment to test Dalton's law.

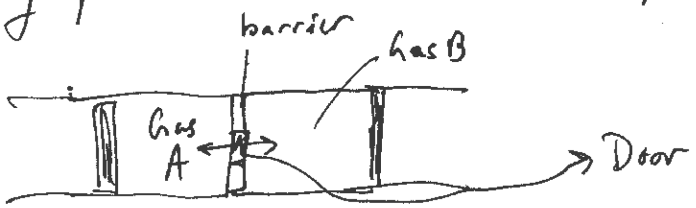
– Dalton's law – the total gas pressure = $\sum_i P_{gas\ i}$ –

(+3) every gas exerts independent partial pressure.

– This makes sense if there is no excluded volume and no (+2) intermolecular attraction – each gas interacts independently with the walls of the container. (+3)

– Many possible answers – for example:

(+3)



Mobile barrier allows pressure to equalize on each side. Then open the door and allow mixing – total pressure should not change.

Score for the page____________

(c; 13 pts) A typical scuba tank holds what was 2200 liters of air at atmospheric pressure, compressed to 200 atm in the tank. Calculate the number of moles of air in the tank and the volume of the tank, assuming 20 °C and ideal gas behavior. What would the pressure in the tank become upon warming it to 40 °C? Approximating air as pure nitrogen N_2 (28 g/mole; don't use this in real diving!), calculate the mass of the gas in a full tank.

2200 L @ 1 atm

(+2) $P_1 V_1 = P_2 V_2$ at constant T

[illegible] (+2) so $V_{tank} = \frac{P_{atm} V_{atm}}{P_{tank}} = \frac{2200}{200} = \underline{11\ L}$

[illegible] & [illegible] (+3) $n = \frac{PV}{RT} = \frac{2200\ L\cdot atm}{0.08206\ L\cdot atm/mole\ K \cdot 293.15 K} = \underline{91.45\ moles}$

(independent of what species of gases are in the air)

(+2) $n = \frac{P_1 V_1}{T_1 R} = \frac{P_2 V_2}{T_2 R}$ so at constant V $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

~~+3~~ (+2) $P_{40°C} = \frac{P_{20°C} \cdot (313.15\ K)}{(293.15\ K)} = 200\ atm \cdot 1.068 = \underline{213.6\ atm}$

(+2) $91.45\ moles \cdot 28\ g/mole = \underline{2560\ g}$

3. Kinetics Reaction Orders (25 pts)

Consider a reaction A ⟶ B that follows first-order kinetics. The integrated rate law is $[A] = [A]_0 e^{-kt}$.

(a; 4 pts) Is this rate law consistent with the reaction being an elementary process? Circle [✓ Yes] or No. (+2)

Does this observed rate law require that the reaction is elementary? Circle Yes or [✓ No]. (+2)

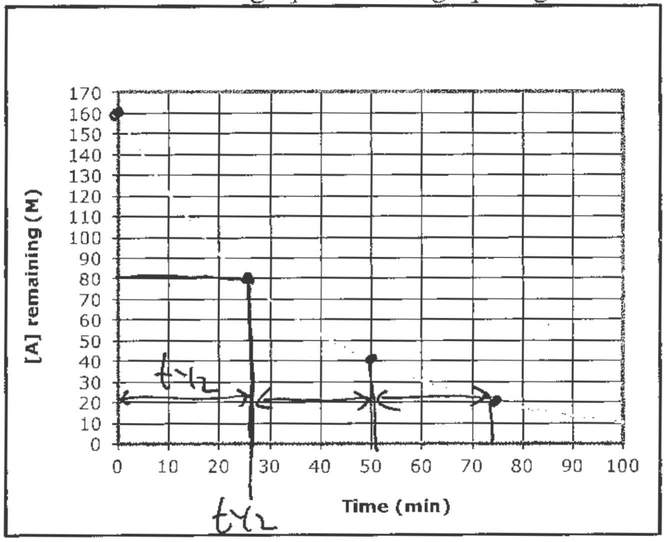
(b; 6 pts) Based on the integrated rate law and the definition of the half life, derive the expression for the half-life $t_{1/2}$ of the reaction as a function of $[A]_0$ and k.

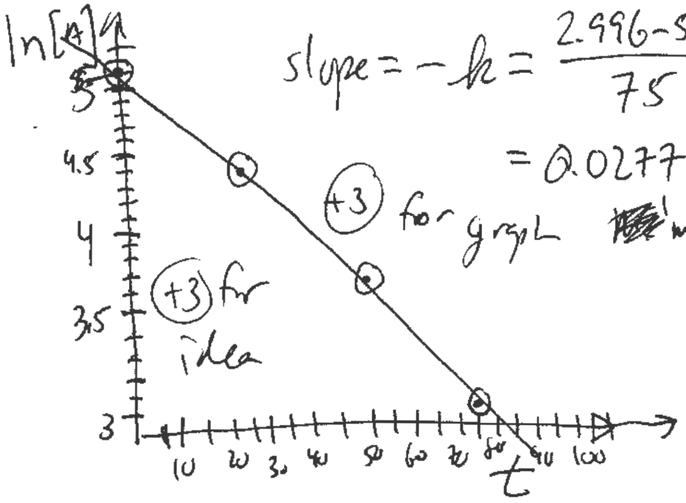
$\frac{[A]_0}{2} = [A]_0 e^{-kt_{1/2}}$ (+3)

$\frac{1}{2} = e^{-kt_{1/2}}$ $\ln(1/2) = -kt_{1/2}$

(+3) $t_{1/2} = \frac{\ln 2}{k}$ indep of $[A]_0$

(c; 15 pts) Consider a time course for this first order reaction sketched at the left below. At the right, create the corresponding linear form graph for the same time course. Determine the half-life and the rate constant from ~~graph~~ one or both graphs: give numerical answers for k and $t_{1/2}$.





(+3) for idea

slope = $-k = \frac{2.996 - 5.075}{75}$

$= 0.0277$ min^{-1}

(+3) for graph

Linear form: $\ln[A] = \ln[A]_0 - kt$ (+3)

$t=0$ $\ln(160) = 5.075$

25 $\ln(80) = 4.382$

50 $\ln(40) = 3.689$

75 $\ln(20) = 2.996$

(+3) $\boxed{t_{1/2} = 25 \text{ min}}$ (or from k)

(+2 each w/out units)

$t_{1/2} = 25$ min

$k = \frac{\ln 2}{t_{1/2}} = \boxed{0.0277 \text{ min}^{-1}}$

(+3) for either method

Score for the page____________

4. Activation Energy and Kinetics (22 pts)

(Adapted from Oxtoby). The rate constant of the elementary reaction below is $k = 1.94 \times 10^{-4}$ at 30 °C. The activation energy E_a is 161 kJ/mol.

$$BH_4^- (aq) + NH_4^+ (aq) \longrightarrow BH_3NH_3 (aq) + H_2 (g)$$

(a; 3 pts) Write down the rate law for this assumed-elementary reaction.

$$\underbrace{\text{Rate} = -\frac{d[BH_4^-]}{dt}}_{+1} = \underbrace{k [BH_4^-][NH_4^+]}_{+2} \quad (+3)$$

(b; 3 pts) What are the units of the rate constant k (and the frequency factor A)?

2nd order - k is in $\underline{M^{-1}sec^{-1}} = M^{-1}/s =$ ~~[illegible]~~ $L/(mol \cdot s)$ (+3)

Note: none of the three parts below require answers to the others.

(c; 4 pts) Calculate the frequency factor A.

$$k = A e^{-E_a/RT}$$

$$1.94 \times 10^{-4} = A e^{-(161000 (J/mol))/(8.314\ J/mol \cdot 303.15\ K)} \quad \Big\} (+2)$$

$$A = \frac{1.94 \times 10^{-4}\ M^{-1}s^{-1}}{e^{-63.87}} = 1.07 \times 10^{24}\ M^{-1}s^{-1} \quad (+2)$$

(which is impossible...)

(d; 6 pts) Calculate the rate constant k at 50 °C.

$$\underbrace{k = (1.07 \times 10^{24}) e^{-(161000/8.314 \cdot 323.15)}}_{(+3) \text{ for plugging in}} = \underbrace{1.011 \times 10^{-2}\ M^{-1}s^{-1}}_{(+3)}$$

Score for the page__________

(e; 6 pts) Calculate the initial rate of reaction at 30 °C for $0.\overset{0}{5}$ M BH_4^- (*aq*) + 0.75 M NH_4^+ (*aq*).

$$\text{Rate} = k\,[0.5\text{ m}](0.75\text{ m})$$ (+3)

$$= 1.94\times10^{-4}\text{ m}^{-1}\text{s}^{-1}\cdot 0.375\text{ m}^2$$

$$\text{Rate} = 7.275\times10^{-5}\ \underline{\text{m}^{-1}\text{s}^{-1}}$$ (+3)

(7.3)

Page	Score
2	/22
3	/18
4	/13
5	/25
6	/16
7	/6
Total	**/100**

Score for the page_______________