Chemistry 271 – 23XX
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General Chemistry and Energetics
Exam I (100 points)

Your Name: Key

Your SID #:

Your Section # or time:

October 10, 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:

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

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

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

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

Integrated rate laws for 0, 1, 2 order:

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

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

Honor Pledge: At the end of the examination time, please write ont 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. Chemical Equilibrium (35 pts)

Methanol is produced industrially by the hydrogenation of carbon monoxide according to the equation below. At room temperature it is a liquid that can be used as fuel.

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

The reaction is accelerated by heterogeneous catalysis on $Cu/ZnO/Al_2O_3$ nanoparticles, on a scale of about 50 million tons MeOH/year. Typical conditions are 300 °C and 100-300 atm total pressure (which requires careful attention to safety). Another challenge is the K_p at this temperature, which is about 3.0×10^{-4} (atm^{-2}). The reaction is somewhat exothermic (produces heat).

(a; 5 pts) Methanol has a molecular weight of 32. Assuming ideal gas behavior (which is far from the truth), what volume would 50 million tons (1 ton = 1000 kg) occupy at 300 °C and 100 atm?

$PV = nRT$ $\frac{50 \times 10^6 \times 10^3 \times 10^3\ g}{32\ g/mol} = \frac{5 \times 10^{13}}{32}\ mol = 1.56 \times 10^{12}$ moles (+1)

(+2) $V = \frac{nRT}{P}$ $= \frac{1.5625 \times 10^{12} \cdot 0.08206\ L\,atm/mol\,K \cdot 573.15\,K}{100\ atm}$ (+1) $= 7.35 \times 10^{11}\ L$ (+1)

$= 7.35 \times 10^8\ m^3$

(~~[illegible]~~ filling a cube tank of ~~[illegible]~~ $\sqrt[3]{\frac{7.35 \times 10^8}{365}} = 126\ m$ on a side every day for a year)

(b; 9 pts) Based on LeChatelier's principle, explain whether the reaction would be driven forward at high vs. low pressure and high vs. low temperature. Explain why the reaction is actually performed at a fairly high temperature.

(+2) 3 moles of gas → 1 mole of gas –

(+1) High pressure ⇒ relieved by ↓ moles of gas → rxn goes forward

(+3) Exothermic ⇒ heat is a product ⇒ ↑ T will drive it backward

There fore it seems that we should do the reaction at lower

(+3) temperature for better yield, but the kinetics are too slow at low T.

(c; 2 pts) Write down the reaction quotient (Q) expression in terms of partial pressures.

$$Q = \frac{P_{CH_3OH}}{P_{CO}\, P_{H_2}^{2}}$$ (+2)

Score for the page /16

(d; 12 pts) For an initial partial pressure of CO of 60 atm and an initial partial pressure of H_2 of 100 atm, with no MeOH initially, do the ICE table and derive the equation that would let you solve for "x", the final partial pressure of MeOH. Calculate the value for "x" assuming that it is << 60 atm. How do you know that this value is physically impossible, beyond just wrong? ~~Why is it so wrong even though K_p is small?~~

(+4)

	P_{CO}	P_{H_2}	P_{CH_3OH}
I	60	~~40~~ 100	0
C	$-x$	$-2x$	$+x$
E	$60-x$	$100-2x$	x

(+3) So $K = 3.0\times10^{-4} = \dfrac{x}{(60-x)(100-2x)^2}$ Cubic. Ick.

(+3) If $x \ll 60$, have $x \cong 3.0\times10^{-4}(60)(100)^2$

$x =$ ~~288 atm~~ 180 atm

(+2) This would give $P_{H_2,\text{final}} =$ ~~40 − 57.6~~ $=$ ~~−17.6~~ no ⊖ pressures

100 − 360 −260

not needed
- The $x \ll 60$ is wrong because 3×10^{-4} is actually not a small number given that there are large pressures raised to the 3rd power on the denominator

(e; 7 pts) It turns out that the true value of x is 25.3 atm. Plug this into your equation and show that it is correct, and calculate the final partial pressures of all three gases. The conversion is far from complete. Speculate on how the % conversion result could be improved industrially, given that K_p is constant.

(+1) $\dfrac{25.3}{(60-25.3)(100-2\cdot25.3)^2} = \dfrac{25.3}{(34.7)(49.4)^2} = 2.98\times10^{-4}$ ✓

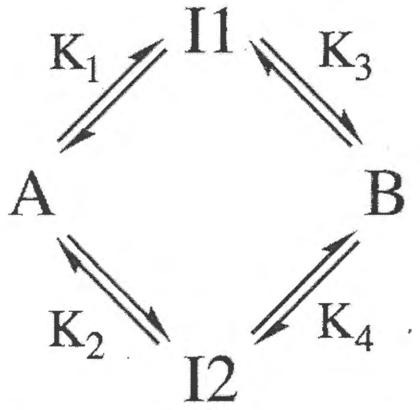
(+3) So $P_{CO} = 34.7$, $P_{H_2} = 49.4$, $P_{CH_3OH} = 25.3$ all in atm

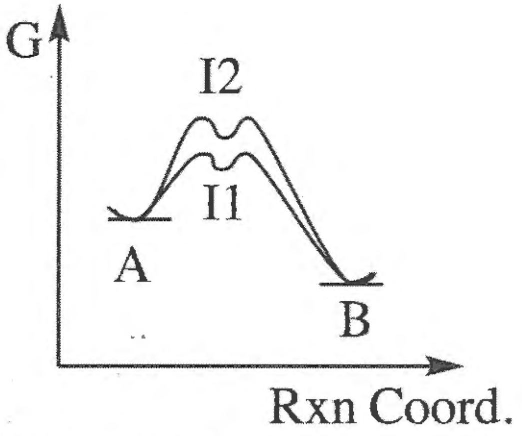
(+3)
- The industrial process either runs at much higher pressure (limited for safety), lower T (too slow), or ~~the~~ CH_3OH is removed in some way – e.g. condensation, or else synthesis is coupled to other more favorable reactions. The syngas is recycled back into the reactor.

Score for the page_____/19

2. Rate Laws (25 pts)

A reaction interconverting A and B can proceed through two pathways, as shown. As the temperature increases, the rates of all elementary reactions increase.





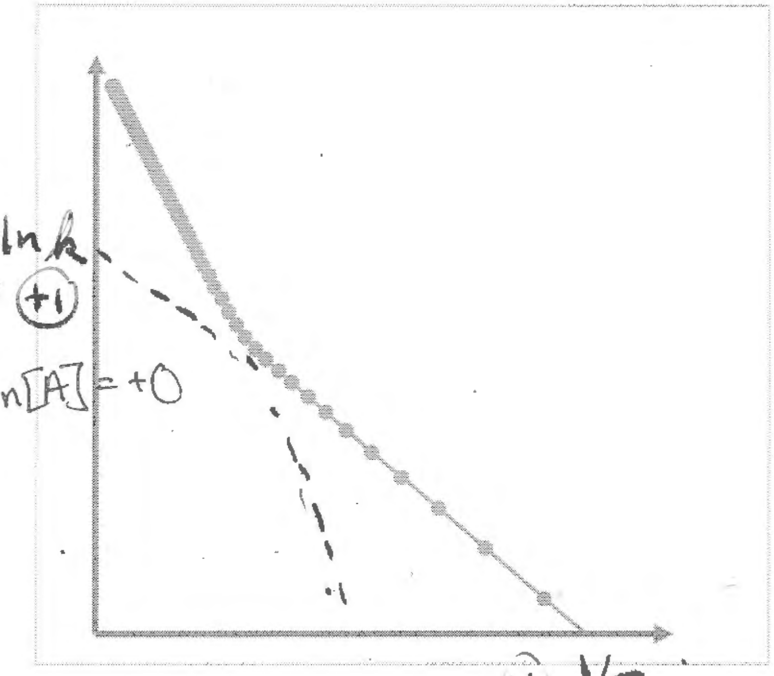
(+2) each

(a; 12 pts) Circle T or F for True/False (2 pts each)

At equilibrium the concentrations of the reactants and products are constant, but the concentrations of intermediates I1 and I2 can continue to change. X	T	[✓ F]
If we know K_1, K_2, and K_3, then we can calculate the value of K_4.	[✓ T]	F
As shown, the activation energies of the two pathways are different. no	[✓ T]	F
Microscopic reversibility says that if the forward process proceeds 98 % via I1 and 2% via I2, then the reverse process must go 98 % through I2, and 2% via I1.	T	[✓ F]
The laws of nature require that the rate of the overall A to B forward reaction increases by the same factor as the rate of the overall B to A reverse reaction (hint: think LeChatelier). Keq [illegible] can change w/ T	T	[✓ F]
Svante Arrhenius was a Dutch chemist. → Swedish	T	[✓ F]

Here is an Arrhenius plot of the observed rate constant just for the forward reaction A -> B discussed above.

(b; 2 pts) Label the axes appropriately (not a trick question).



ln k (+1)

ln[A] = +0

(+1) 1/T

(c; 3 pts) What does the slope of an Arrhenius plot represent?

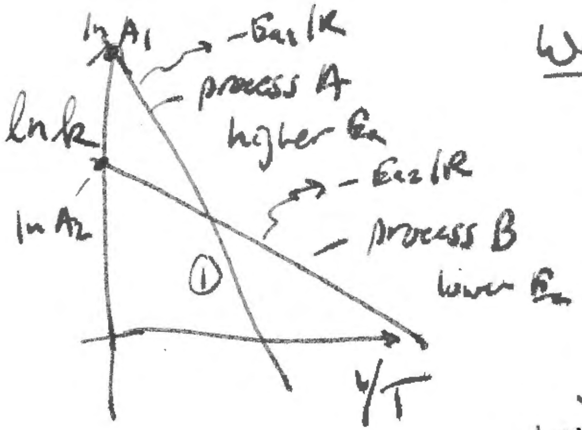
(+3) slope = $-E_a/R$
activation energy

E_a / K = +2

Score for the page /17

(d; 8 pts) Propose an explanation for the bend in the Arrhenius plot in terms of the intermediates I1 and I2 and the corresponding Arrhenius equation parameters.

If the two processes have different activation energies (+3) and pre-exponential factors, then we can ~~have~~ observe the dominant mechanism switching as T changes. (+3)



We observe the faster process. So it looks like I_1 has a lower E_a and lower A, I_2 has higher E_a and higher A – as T ↑, I_2 increases.

we observe the sum, which is dominated by the faster process (+2)

3. Ideal and Non-ideal Gases (19 pts)

(a; 6 pts) What are the two assumptions that we make in applying the ideal gas law to real gases (what two properties of a real gas do we neglect)?

- No excluded volume. (+3)
- No inter-molecular interactions (+3)

more ideal at low P and high T

gases stay gasses +2

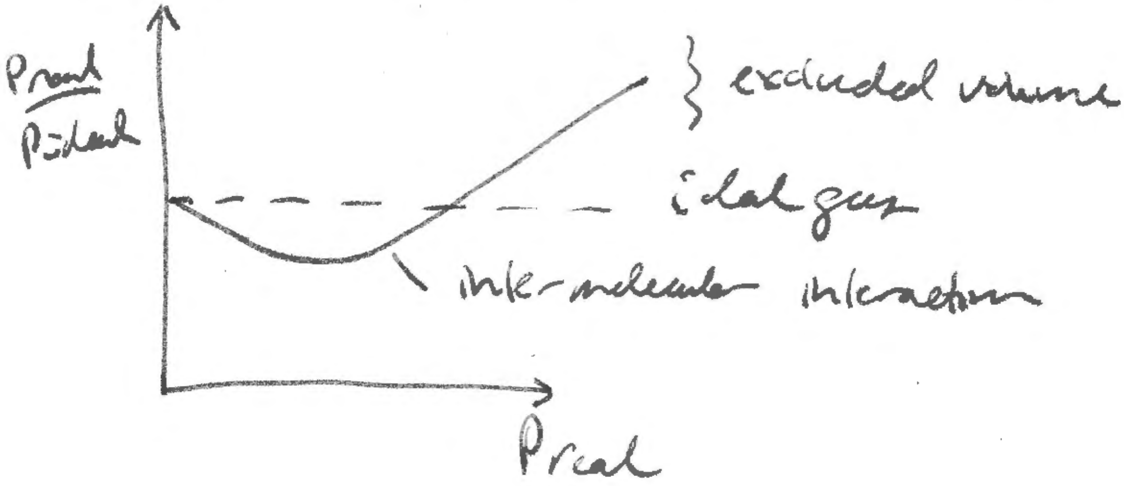
(b; 4 pts) We characterize deviations from ideal gas behavior by graphing $P_{real}V/nRT$. Show that this is the same as P_{real}/P_{ideal}.

$P_{ideal} \cdot V = nRT$ so $P_{ideal} = \frac{nRT}{V}$ → (+1)

$\frac{P_{real}}{P_{ideal}} = \frac{P_{real}}{(nRT/V)} = \frac{P_{real} \cdot V}{nRT}$ ✓ (+3)

Score for the page / 18

(c; 9 pts) Sketch a graph ($P_{real}V/nRT$) vs. the actual pressure P_{real} for (1) an ideal gas and (2) methane. Methane has significant intermolecular attractions, but we are at a temperature high enough so that it does not liquefy. Identify the features of the graph relating to each of the two assumptions in (a).



+2 for idea

+1 for ideal gas

+2 for shape of curve

+2 for excluded volume ↑ P_{real}

+2 for inter-molecular attraction ↓ P_{real}

Score for the page /9

with respect to A and B individually

4. Kinetics (21 pts)

Consider the irreversible but possibly complicated reaction A + B → C + D. You perform several time courses to establish the rate law. The initial rate of reaction at 0.5 M [A] and 0.75 M [B] is 80 Ms^{-1}.

(a; 6 pts) When you double both [A] and [B] the initial rate increases by a factor of 4. Does this fact alone tell you the reaction orders? Why or why not?

No – it could be 2nd order in A and zero order in B or vice versa – cannot predict a rate law from stoichiometry unless the reaction is elementary.

(+2) (+4) (+2)

or any combination of orders that sum to 2.

max possible = 6

(b; 3 pts) When you double the concentration of B (leaving [A] alone) the initial rate doubles. What is the reaction order with respect to B?

$\text{Rate} = k[A]^x[B]^y$

Must have $y=1$ – first order in B (+3)

(c; 6 pts) When B is present in large excess (hint: "pseudo" conditions) and you measure the half-life of A in the reaction mix, you find that the half-life is independent of [A]. What does $\boxed{\text{this alone}}$ tell you about the reaction orders for A and for B?

(+3)

– half-life independent of [A] ⇒ first order in [A].

$t_{1/2} = \ln 2/k$, or really $\ln 2/(\underbrace{k[B]^y}_{\text{constant}})$

[If [B] is small enough to change noticeably, then the $t_{1/2}$ for [A] will ↑ as the rxn progresses]

– So we learn nothing about rxn order w.r.t. B from this one expt. unless we repeat at many [B].

(+3)

(+1 if refer to prev. knowledge of B)

Score for the page____________

(d; 6 pts) Combining everything you know from (a)-(c), write down the rate law and the rate constant, with units.

↳ calculate

(+2)

$$\underline{\text{Rate} = k[A]^1[B]^1} = -\frac{d[A]}{dt}$$

$$\text{so } 80\ \text{Ms}^{-1} = k(0.5\,\text{M})(0.75\,\text{M})\ \Big]\ (+2)$$

$$k = \frac{80}{\frac{1}{2}\cdot\frac{3}{4}} = \frac{640}{3} = \underline{\overset{213^{+1}}{\cancel{2133}}\ \overset{+1}{\text{M}^{-1}\text{s}^{-1}}}\ (+2)$$

2nd order

(210 and 2 sig figs ok)

full credit if consistent w/ Rate law

Page	Score
2	/16
3	/19
4	/17
5	/18
6	/9
7	/15
8	/6
Total	**/100**

Score for the page 16