Chemistry 271 – 22XX
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General Chemistry and Energetics
Exam I (100 points)

Your Name: - Key -

Your SID #:

Your Section # or time:

March 1, 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.

N=150+3+1

Useful Equations:

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

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

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

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

$K_p = K_c(RT)^{\Delta n}$ Mass of H: 1.008 g/mole $E = mc^2$

Integrated rate laws for 0, 1, 2 order:

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

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

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

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."

1. Chemical Equilibrium and Gas Laws (40 pts)

The equilibrium constant for the endothermic reaction $H_2(g) + I_2(s) \rightleftharpoons 2\ HI(g)$ is $K_c = 1.37 \times 10^{-4}$, at 25 °C.

wrong – should have been 1.41×10^{-2}

(a; 8 pts) Write down the reaction quotient Q expression in terms of partial pressures, and calculate the value of K_p at 25 °C.

[Actual $K_p = 0.345$]

~~$Q = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$~~ ← if solid included (+1)

if conc +1 →

$$Q = \frac{(P_{HI})^2}{P_{H_2}} \quad (+3)$$

Δn = change in moles of gas = +1 (+1)

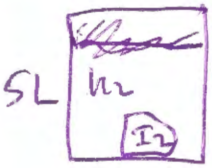
$$\overset{(atm)}{K_p} = \overset{(M)}{K_c}(RT)^{\Delta n} = 1.37\times10^{-4}(0.08206\ L\cdot atm/mol\ K \cdot 298.15\ K)^{+1} \quad (+2)$$

$$= 3.35\times10^{-3}\ (atm) \quad (+2)$$

math error (+1)

[+5 if R = 8.314 is used, and then full credit below for using $K_p = 0.345$] → oops…

(b; 12 pts) Gaseous H_2 is added to excess solid iodine in a 5 L container, and the equilibrium partial pressure at 25 °C of H_2 is found to be $P_{H2} = 0.92$ atm. Calculate the number of moles and the mass of H_2 that are present at equilibrium. What is the equilibrium partial pressure of HI? What is the ratio of (the average kinetic energy per molecule of the HI molecules)/(the average kinetic energy per molecule of the H_2 molecules)?



+1 if calc'd HI

eq. PV=nRT then (+1) ←

$$P_{H_2} = 0.92\ atm = \frac{n}{V}\cdot RT$$

$$n = \frac{PV}{RT} = \frac{(0.92\ atm)(5\ L)}{(0.08206\ L\cdot atm/mol\ K)(298\ K)} = \underline{0.188\ moles\ H_2} \quad (+3)$$

math error (+1)

$$0.188\ moles \times 2.016\ g/mol\ H_2 = \underline{0.379\ g\ H_2} \quad (+2)$$

(+1 for using 1 g/mol) 2 g/mol (–1)

wrong ratio math (–1)

just ICE table (+1)

$$\underline{3.35\times10^{-3}\ atm = \frac{P_{HI}^2}{P_{H_2}}} \quad (+2)(+1)$$

$$so\quad P_{HI} = (3.35\times10^{-3}\cdot 0.92)^{1/2} = \underline{5.55\times10^{-2}\ atm}$$

(+2) (+2) 2nd O.

[full credit for $P_{HI} = (0.345 \times 0.92)^{1/2} = 0.563$ atm]

$$\frac{(Avg.\ KE\ of\ HI)}{(Avg.\ KE\ of\ H_2)} = \underline{1} \quad (+2)$$

because they are at the same temperature

Score for the page /20

(c; 12 pts) Excess solid I_2 is added to a separate 5 L container initially filled with 3.80 atm of H_2, with the vessel maintained at constant volume and 25 °C. How do you know in advance that the final total pressure in the container will be more than 3.80 atm? Set up but do not solve the quadratic equation that would give you the final partial pressure of HI.

-If a mole of H_2 reacts, 2 moles of HI are produced - so the overall pressure must increase. The change in volume from using up I_2 is negligible.

(+2)

R	H_2 +	$I_2 \rightarrow$	$2HI$
I	3.80 atm	(xs)	0
C	$-x$	$(-x)$	$+2x$
E	$3.80-x$	(xs)	$2x$

(+3)

$$K_p = 3.35\times10^{-3} = \frac{P_{HI}^2}{P_{H_2}} = \frac{(2x)^2}{3.80-x}$$

(+4)

so +7 for this

$$4x^2 - (3.35\times10^{-3})(3.80-x) = 0$$

(+3)

(gives $x =$ ~~[illegible]~~ 0.174 atm, total P = 3.974; correct ans is $x = 0.531$, P = 4.331 atm)

(d; 3 pts) How would the partial pressures change if more excess solid I_2 were added to either container?

It does not change - pure solids do not appear in the Q expression

(+3)

(e; 5 pts) If the volume of either container is increased at constant temperature, which way will the equilibrium shift? If the temperature is increased, will the equilibrium constant increase or decrease?

-If V↑ at constant T, P↓ and the system will shift to the right to increase the pressure.

(+3)

-The reaction is endothermic, so as T↑, K↑.

(+2)

Score for the page /20

2. Chemical Kinetics (48 pts)

The Zeldovich mechanism describes the oxidation of N_2 gas by O_2 in internal combustion engines, which is a source of smog. Here is the overall reaction:

$N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$ for which the observed rate law is $\frac{d[\mathrm{NO}]}{dt} = k[\mathrm{O_2}]^{1/2}[\mathrm{N_2}]$

(a; 6 pts) How do you know from just glancing at the rate law that the reaction is not elementary? What are the units of the *k* in the rate law?

- The elementary reaction would have rate law, $\frac{1}{2}\frac{d[NO]}{dt} = k[N_2][O_2]$, which does not match the rate law given (+3) not needed

- $\frac{d[NO]}{dt}$ has units of M/s so k must be in $M^{-1/2}s^{-1}$ (+3)

We will evaluate a simplified version of the proposed mechanism. First, we assume that O atoms are produced by collisions between molecular O_2 and collision gas M, at the high temperature of the combustion chamber (~2000 K), according to the reaction below, so that O atoms are maintained at a constant pseudo-equilibrium concentration:

$$O_2(g) + M \overset{K_O}{\rightleftarrows} O(g) + O(g) + M$$

(b; 5 pts) Solve for [O] as a function of [O_2] and K_O. Not a trick question.

$$K_O = \frac{[O]^2[M]}{[O_2][M]} \quad \text{so} \quad [O] = \sqrt{K_O[O_2]}$$

(+3) (+2)

Here are the two steps for N_2 oxidation. The nitrogen atom N is treated as a steady state intermediate.

Step 1	$O\ (g) + N_2\ (g) \rightarrow NO\ (g) + N\ (g)$	Slow, rate constant k_1
Step 2	$N\ (g) + O_2\ (g) \rightarrow NO\ (g) + O\ (g)$	Fast, rate constant k_2

(c; 6 pts) Write down the differential rate law for the formation of NO as a function of [O], [O_2], [N], [N_2], and *k*'s.

(+2) for idea of a rate law

$$\frac{d[NO]}{dt} = \underbrace{k_1[O][N_2]}_{(+2)} + \underbrace{k_2[N][O_2]}_{(+2)}$$

Score for the page /17

(d; 11 pts) Write down the differential rate law for [N]. Solve for the steady state [N] as a function of $[N_2]$, [O], $[O_2]$, and k's. Explain why the second step must to be fast for us to apply the SSA.

$$\underbrace{\frac{d[N]}{dt} = k_1[O][N_2] - k_2[N][O_2]}_{(+3)} \underset{\uparrow \text{SSA}}{=} 0 \quad (+1)$$

$$k_2[N][O_2] = k_1[O][N_2] \quad \text{so} \quad [N] = \frac{k_1[O][N_2]}{k_2[O_2]} \quad (+4)$$

– To apply the SSA, the intermediate must have a rapid decay path, and the second step is the decay step.

(+3) (+1)

(e; 13 pts) Substitute your answers for (b) and (~~c~~ d) into your oops answer for (~~d~~ c) to give the rate law for NO as a function of $[N_2]$, $[O_2]$, K_O, and k's. Hint: at the beginning of the problem I told you what it should look like. Explain why your answer does not (or should not) include the rate constant k_2 or the concentrations of [N] and [O].

$$\frac{d[NO]}{dt} = k_1[O][N_2] + k_2[N][O_2]$$

(+4) for idea

$$= k_1\underbrace{\left(\sqrt{K_O[O_2]}\right)}_{[O]}[N_2] + \cancel{k_2}\overbrace{\left(\frac{k_1\sqrt{K_O[O_2]}\,[N_2]}{\cancel{k_2}\,\cancel{[O_2]}}\right)}^{[N]}\cancel{[O_2]}$$

$$= k_1 K_O^{1/2}[O_2]^{1/2}[N_2] + k_1 K_O^{1/2}[O_2]^{1/2}[N_2]$$

(+4)

$$\frac{d[NO]}{dt} = \boxed{2k_1K_O^{1/2}}[O_2]^{1/2}[N_2]$$

→ "k" in the rate law given

• "k_2" does not appear b/c it is the k for a fast step after the rate determining step, and [N] ~~and [O]~~ are intermediates, so should not appear, [O] doesn't because it's constant and we express it in terms of $[O_2]$.

(+3) (+2)

Score for the page_________ /24

would get 3.95×10^{10} for 2000 K
3.73×10^{10} for 500 K

(f; 7 pts) Indepeudent question: The activation energy for the rate limiting step (k_1) is 314 kJ/mole, and the pre-exponential factor A = 4.03 x 10^{10} (with appropriate units). What is the rate constant k_1 at 2000 K? What is it at 500 K?

if used 314 J
instead of 314000 J
then 4/7

Front of exam gives $\ln k = \ln A - \frac{E_a}{RT}$

$k = Ae^{-E_a/RT}$

(+3) { $k =$ ~~314×10^3~~ $(4.03\times10^{10}\ M^{-1/2}s^{-1})(e^{-314000\ J/mol / 8.314\ J/mol\ K \cdot T(K)})$

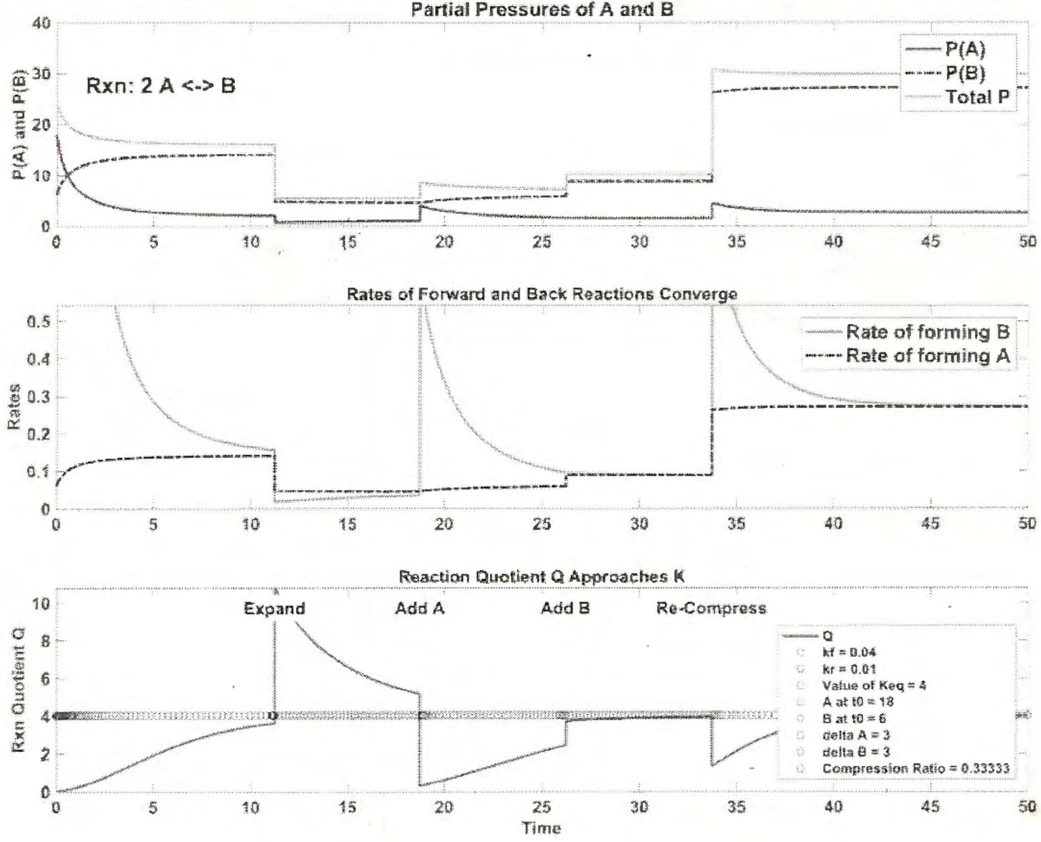
for T = 2000 K, $k = 4.03\times10^{10}\ e^{-18.884} = \underline{254\ M^{1/2}s^{-1}}$ (+2)

for T = 500 K, $k =$ " $e^{-75.5} = \underline{6.32\times10^{-23}}\ M^{-1/2}s^{-1}$ (+2)

(This is why we don't worry too much about the atmosphere spontaneously converting to nitric oxide)

3. LeChatelier's principle (12 pts)

Here is a picture like the ones we looked at in class, generated using Matlab, for the reaction 2 A ⇌ B.



Score for the page 17

instantaneously

(a; 12 pts) At time 18, we add more "A" to the reaction mixture – note that the P(A) line in the top panel pops up. Explain (i) why the "Rate of forming B" line in the middle panel increases rapidly, (ii) why it subsequently decays, and (iii) why the line for "Rate of Forming B" changes (up and down) so much more markedly than the line for "Rate of Forming A" throughout the middle panel. Finally, (iv) explain why the value of Q decreases upon compression at 33 min.

(+2) (i) We have added A, so the rate of forming B pops up rapidly

(+2) (ii) As A is progressively converted to B, the rate ~~of~~ of $2A \rightarrow B$ decreases (and the rate of $B \rightarrow 2A$ increases).

(+4) (iii) Because $2A \rightarrow B$ is second order and $B \rightarrow 2A$ is first order, the rate for the forward reaction is much more sensitive to changes in concentration

(+4) (iv) $Q = \frac{P_B}{(P_A)^2}$ so upon compression by "n-fold",

we have $Q \rightarrow \frac{P_B \cdot n}{(P_A)^2 \cdot n^2} = \frac{1}{n} \cdot$ original Q

(OK to just say "denominator increases more than numerator")

Page	Score
2	/20
3	/20
4	/17
5	/24
6	/7
7	/12
Total	**/100**

Score for the page /12