Chemistry 271 – 22XX
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General Chemistry and Energetics
Exam 1 (100 points)

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:

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

Integrated rate laws for 0, 1, 2 order:

\[ \frac{[A]}{[A]_0} = 1 - kt \]
\[ \ln[A] = \ln[A]_0 - kt \]
\[ t_{1/2} = \frac{0.693}{k[A]_0} \]

\[ N = R_v \cdot f_p \cdot n_e \cdot f_t \cdot f_i \cdot f_c \cdot L \]

\[ PV = nRT \]

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 \( \text{H}_2(g) + \text{I}_2(s) \rightleftharpoons 2 \text{HI}(g) \) is \( K_c = 1.37 \times 10^{-4} \) at 25 °C.

(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.

\[
Q = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}P_{\text{I}_2}}
\]

\[
K_p = K_c \frac{(RT)^{\Delta n}}{\Delta n}
\]

\[
= 3.35 \times 10^{-3} \text{ atm}^2
\]

(b; 12 pts) Gaseous \( \text{H}_2 \) is added to excess solid iodine in a 5 L container, and the equilibrium partial pressure at 25 °C of \( \text{H}_2 \) is found to be \( P_{\text{H}_2} = 0.92 \text{ atm} \). Calculate the number of moles and the mass of \( \text{H}_2 \) that are present at equilibrium. What is the equilibrium partial pressure of \( \text{HI} \)? What is the ratio of (the average kinetic energy per molecule of the \( \text{HI} \) molecules)/(the average kinetic energy per molecule of the \( \text{H}_2 \) molecules)?

\[
P_{\text{H}_2} = 0.92 \text{ atm} = \frac{n}{V}RT
\]

\[
n = \frac{PV}{RT} = \frac{(0.92 \text{ atm})(5 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 0.188 \text{ moles H}_2
\]

\[
0.188 \text{ moles} \times 2.016 \text{ g mol}^{-1} \text{ H}_2 = 0.379 \text{ g H}_2
\]

\[
P_{\text{HI}} = \frac{3.35 \times 10^{-3} \text{ atm}}{0.92 \text{ atm}} = 5.55 \times 10^{-2} \text{ atm}
\]

\[
\left( \frac{\text{Avg. KE (HI)}}{\text{Avg. KE (H}_2)\right) \right) = 1 \text{ because they are at the same temperature}
\]

Score for the page: 120
(c; 12 pts) Excess solid I₂ is added to a separate 5 L container initially filled with 3.80 atm of H₂, 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 H₂ reacts, 2 moles of H₂ are produced - so the overall pressure must increase. The change in volume from using up I₂ is negligible.

R: \[ H₂ + I₂ \rightarrow 2HI \]

I: \[ 3.80 \text{ atm (x)} \cdot 0 \]

C: \[ -x \ (-x) + 2x \]

E: \[ 3.80 - x \ (x) \ 2x \]

\[ K_p = 3.35 \times 10^{-2} = \frac{p_{HI}^2}{p_{H₂}} = \frac{(2x)^2}{3.80 - x} \]

\[ 4x^2 - (3.35 \times 10^{-2})(3.80 - x) = 0 \]

\[ (1) \]

(d; 3 pts) How would the partial pressures change if more excess solid I₂ were added to either container?

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

(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.

- The reaction is endothermic, so at T↑, K↑.
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:

\[
N_2 (g) + O_2 (g) \rightarrow 2 \text{NO} (g)
\]

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

(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?

(b; 5 pts) Solve for \([O]\) as a function of \([O_2]\) and \(K_0\). Not a trick question.

\[
K_0 = \frac{[O]^2 [M]}{[O_2] [M]}
\]

so \([O] = \sqrt{K_0 [O_2]}\)

(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.
(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 be fast for us to apply the SSA.

\[
\frac{d[N]}{dt} = k_1 [O][N_2] - k_2 [N][O_2] = 0 (\text{SSA})
\]

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

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

(c; 13 pts) Substitute your answers for (b) and (d) into your answer for (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 \([O]\).

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

\[
= k_1 (\sqrt{K_0 [O_2]}) [N_2] + k_2 \left( \frac{k_1 \sqrt{K_0 [N_2]}}{k_2 [O_2]} \right) [O_2]
\]

\[
= k_1 K_o^{1/2} [O_2]^{1/2} [N_2] + k_2 K_o^{1/2} [O_2]^{1/2} [N_2]
\]

\[
(4) \quad \frac{d[NO]}{dt} = 2 k_1 K_o^{1/2} [O_2]^{1/2} [N_2]
\]

"\(k_2\) does not appear \(b/c\) it is the \(k\) for a fast step. After the rate determining step, and \([N]\) and \([O]\) don't appear, \([O]\) doesn't because it's constant, and we express it in terms of \([O_2]\)."

score: 24
(f; 7 pts) Independent question: The activation energy for the rate limiting step \((k_f)\) is 314 kJ/mole, and the pre-exponential factor \(A = 4.03 \times 10^{10}\) (with appropriate units). What is the rate constant \(k_f\) at 2000 K? What is it at 500 K?

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

\[
k = A e^{-\frac{E_a}{RT}}
\]

\[
(+) \quad k_2 = 3.14 \times 10^{10} (4.03 \times 10^{10} \text{ m}^{-\frac{1}{2}} \cdot \text{s}^{-1}) (e^{-314000 \text{ J/mol}/(8.314 \cdot \text{mol} \cdot \text{K} \cdot \text{K})})
\]

for \(T = 2000 \text{ K}, \quad k_f = 4.03 \times 10^{10} e^{-18.884} = 254 \text{ m}^{\frac{1}{2}} \cdot \text{s}^{-1}\)

for \(T = 500 \text{ K}, \quad k_f = e^{-755} = 6.32 \times 10^{-23} \text{ m}^{\frac{1}{2}} \cdot \text{s}^{-1}\)

(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 \(2 \text{ A} \rightleftharpoons \text{ B}\).
(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.

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

(ii) As A is progressively converted to B, the rate of \( \text{B} \rightarrow \text{A} \) decreases (and the rate of \( \text{B} \rightarrow \text{B} \) increases).

(iii) Because \( \text{B} \rightarrow \text{B} \) is second order and \( \text{B} \rightarrow \text{A} \) is first order, the rate for the forward reaction is much more sensitive to changes in concentration.

(iv) \( Q = \frac{P_B}{(P_A)^2} \) so upon compression by “N-fold”,
we have \( Q \rightarrow \frac{P_B \cdot N}{(P_A)^2 \cdot N^2} = \frac{1}{N} \cdot \text{original Q} \)

(OK to just say “denominator increase more than numerator.”)

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