Chemistry 271 – 23XX

Prof. Jason Kahn

University of Maryland, College Park

General Chemistry and Energetics

Exam I (100 points)

Your Name: ____________________________________________

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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:

\[ K_a = [H^+][A^-]/[HA] \]

\[ pH = -\log([H^+]) \]

\[ (P-nb)(P+an^2/V^2) = nRT \]

\[ R = 0.08206 \text{ L·atm/mole K} \]

\[ k_B = 1.38 \times 10^{-23} \text{ J/K} \]

\[ \text{ln}K_{eq} = -\Delta H^\circ/(RT) + \Delta S^\circ/R \]

\[ R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_Ak_B \]

\[ \text{In} \ k = (-E_a/RT) + \ln A \]

\[ ^\circ C = ^\circ K - 273.15 \]

\[ P(v)dv = Cv^2\exp(-mv^2/2kT) \]

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

Integrated rate laws for 0, 1, 2 order:

\[ [A] = [A]_0 - kt \]

\[ \ln[A] = \ln[A]_0 - kt \]

\[ 1/[A] = 1/[A]_0 + 2kt \]

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

\[ t_{1/2} = \ln 2/k \]

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

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. **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.

\[ \text{CO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \]

The reaction is accelerated by heterogeneous catalysis on Cu/ZnO/Al\(_2\)O\(_3\) 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 \(\times\) 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?

(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.

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

(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.
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.

![Diagram of reaction pathways]

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

<table>
<thead>
<tr>
<th>Statement</th>
<th>True</th>
<th>False</th>
</tr>
</thead>
<tbody>
<tr>
<td>At equilibrium the concentrations of the reactants and products are constant, but the concentrations of intermediates I1 and I2 can continue to change.</td>
<td>T</td>
<td>F</td>
</tr>
<tr>
<td>If we know K₁, K₂, and K₃, then we can calculate the value of K₄.</td>
<td>T</td>
<td>F</td>
</tr>
<tr>
<td>As shown, the activation energies of the two pathways are different.</td>
<td>T</td>
<td>F</td>
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<tr>
<td>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.</td>
<td>T</td>
<td>F</td>
</tr>
<tr>
<td>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).</td>
<td>T</td>
<td>F</td>
</tr>
<tr>
<td>Svante Arrhenius was a Dutch chemist.</td>
<td>T</td>
<td>F</td>
</tr>
</tbody>
</table>

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).

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

Score for the page__________
(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.

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)?

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

Score for the page___________
(c; 9 pts) Sketch a graph \((P_{\text{real}}V/\text{nRT})\) vs. the actual pressure \(P_{\text{real}}\) 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).
4. Kinetics (21 pts)
Consider the irreversible but possibly complicated reaction $A + B \rightarrow C + D$. 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 $80 \, \text{Ms}^{-1}$.

(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?

(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 $B$?

(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 this alone tell you about the reaction orders for $A$ and for $B$?
(d; 6 pts) Combining everything you know from (a)-(c), write down the rate law and the rate constant, with units.