Midterm Examination 2

Useful Information is Located at the End of the Exam.

Multiple Choice Questions

1. An Elementary Step in a reaction mechanism tells us:
   a) how many moles of each reagent are required for the chemical reaction to proceed.
   b) **which molecules collide and react. ***
   c) how the molecules have to be oriented in the Transition State.

2. A catalyst:
   a) does not participate in a chemical reaction.
   b) increases the Activation Energy of the slowest step in the Mechanism.
   c) **provides an alternate pathway for the reaction; one with lower Activation Energies.***
   d) is permanently changed during the course of the chemical reaction.

3. What is the molecularity of the following Elementary Reaction Step?
   \[ \text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2 \]
   a) Unimolecular
   b) **Bimolecular***
   c) Termolecular
4. The reaction of Ethylene and Hydrogen occurs in the presence of a catalytic metal, such as Platinum or Gold:

\[
\text{CH}_2\text{-CH}_2(g) + \text{H}_2(g) \rightarrow \text{CH}_3\text{-CH}_3(g)
\]

This reaction is first order at low Hydrogen concentrations but zeroth order at higher Hydrogen concentrations. This is because:

a) the H-H bond becomes weaker due to a greater number of collisions at higher concentrations.
b) the product decomposes more readily at higher concentrations.
c) the active sites on the metal become saturated at higher concentrations.  

5. The value of \( K_c \) for the following reaction at 900°C is 0.28:

\[
\text{CS}_2(g) + 4 \text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + 2 \text{H}_2\text{S(g)}
\]

What is the value of \( K_p \) at this temperature?

a) \( 3.0 \times 10^{-5} \)  

\[
\Delta n_g = 3 - 5 = -2
\]

b) \( 2.1 \times 10^{-4} \)

c) \( 6.7 \times 10^{-3} \)

d) \( 1.4 \times 10^{-2} \)

\[
K_p = K_c (RT)^{\Delta n_g} = (0.28) ((0.08206) (1173))^{-2} = 3.0 \times 10^{-5}
\]

6. The equilibrium constant for the reaction:

\[
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI(g)}
\]

is \( K_c = 50.75 \). What is \( K_c \) for the following reaction:

\[
\text{HI(g)} \rightleftharpoons \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{I}_2(g)
\]

a) 3.45

\[
K_c = 1 / (50.75)^{1/2} = 0.14
\]

b) \( 0.14 \)

\[
K_c = 1 / (50.75)^{1/2} = 0.14
\]

c) 0.028

d) 0.0079
7. At 425°C, \( K_P = 4.18 \times 10^{-9} \) for the reaction:

\[
2 \text{HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g)
\]

If we introduce each of these gases into a container at 425°C at partial pressures of:

\[
\begin{align*}
P_{\text{HBr}} &= 0.20 \text{ atm} \\
P_{\text{Br}_2} &= 0.0010 \text{ atm} \\
P_{\text{H}_2} &= 0.0010 \text{ atm}
\end{align*}
\]

In which direction will this reaction proceed?

a) **Toward Reactants.** \( Q = \frac{P_{\text{H}_2} P_{\text{Br}_2}}{P_{\text{HBr}}^2} = \frac{(0.0010)(0.0010)}{(0.20)^2} = 2.5 \times 10^{-5} \)

b) Toward Products.

c) Neither direction, it is at equilibrium.

\[ Q > K_P \]

8. The following system is allowed to come to equilibrium:

\[
\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)
\]

Additional PCl₅ is added to the system. The system will:

a) **respond by shifting to the Left.**

b) respond by shifting to the Right.

c) not be affected.

9. The pOH of a solution that has \([\text{H}^+] = 5 \times 10^{-5} \text{ M}\) is:

a) 8.6 \[ \text{pH} = -\log(5 \times 10^{-5}) = 4.30 \]

b) **9.7**

c) 10.5 \[ \text{pOH} = 14 - \text{pH} = 14 - 4.30 = 9.70 \]

d) 11.7

10. Which of the following is a strong acid?

a) HF

b) **HClO₄**

c) HOCl

d) NH₃
11. For the following acid-base reaction:

\[ \text{HPO}_4^{2-}(aq) + \text{NH}_4^+(aq) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{NH}_3(aq) \]

The base is:

a) \text{HPO}_4^{2-} ***** It is the H\(^+\) acceptor.
b) \text{NH}_4^+
c) \text{NH}_3
d) \text{H}_2\text{PO}_4^-

12. In the following reaction:

\[ \text{Ni(s)} + 4 \text{CO(g)} \rightarrow \text{Ni(CO)}_4(g) \]

The Lewis base is:

a) \text{Ni}
b) \text{CO} ***** Donates an e\(^-\) to the Ni to form the Ni-CO bond.
c) \text{Ni(CO)}_4
d) none of these species is basic.

13. How many milliliters of Concentrated HCl (12 M) is required to prepare 5 L of a solution that has a pH = 1?

a) 42 ***** \( \text{pH} = -\log[\text{H}^+] \) or \( [\text{H}^+] = 10^{-\text{pH}} = 10^{-1} = 0.01 \text{ M} \)
b) 27
c) 10 \( \text{V}_2 = \text{M}_1 \text{ V}_1 / \text{M}_2 = (0.01 \text{ M}) (5000 \text{ mL}) / (12 \text{ M}) = 42 \text{ mL} \)
d) 3

14. 0.75 g of gaseous HCl is bubbled into enough Water to prepare 500 mL of a Hydrochloric Acid solution. What is the pH of the solution?

a) 12.8 \# \text{mol HCl} = (0.75 \text{ g}) (1 \text{ mol HCl} / 36.5 \text{ g}) = 0.0205 \text{ mol HCl} = 0.0205 \text{ mol H}^+
b) 10.7
c) 8.1
d) 1.4 ***** \([\text{H}^+] = (0.0205 \text{ mol}) / (0.500 \text{ L}) = 0.0411 \text{ M} \)
\( \text{pH} = -\log(0.0411) \) 1.4
15. What is the pH of a 0.50 M Nitrous Acid, HNO₂, solution? $K_a = 7.1 \times 10^{-4}$ for Nitrous Acid.

a) 6.22  
b) 3.45  
c) **1.72***  
d) 0.87

\[
\begin{align*}
\text{HNO}_2 & = \text{H}^+ + \text{NO}_2^- \\
\text{I} & \quad 0.50 \text{M} \quad 0 \text{M} \quad 0 \text{M} \\
\text{C} & \quad - x \quad + x \quad + x \\
\text{E} & \quad 0.50 - x \quad x \quad x \\
\end{align*}
\]

\[K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}\]

\[7.1 \times 10^{-4} = \frac{x^2}{(0.50 - x)} \sim \frac{x^2}{0.50}\]

\[x = [\text{H}^+] = 0.0188 \text{ M}\]

\[\text{pH} = - \log(0.0188) = 1.72\]
Short Answer

1. The oxidation of Nitric Oxide by Oxygen:

\[
2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2
\]

is thought to proceed in a two step mechanism:

\[
\begin{align*}
\text{NO} + \text{O}_2 & \rightleftharpoons \text{NO}_3 \quad \text{(fast)} \\
\text{NO}_3 + \text{NO} & \rightleftharpoons 2 \text{NO}_2 \quad \text{(slow)}
\end{align*}
\]

What is the rate law for this reaction as predicted by this mechanism assuming the "Equilibrium" Approximation can be applied to the first step in this mechanism? (You must show your work.)

\[
\text{Rate} = k_2 [\text{NO}_3][\text{NO}]
\]

Apply the Equilibrium Approximation

\[
\begin{align*}
\text{Rate}_1 &= \text{Rate}_1 \\
k_1 [\text{NO}][\text{O}_2] &= k_{-1} [\text{NO}_3]
\end{align*}
\]

Solving:

\[
[\text{NO}_3] = \left(\frac{k_1}{k_{-1}}\right)[\text{NO}][\text{O}_2]
\]

\[
\text{Rate} = \left(\frac{k_1 k_2}{k_{-1}}\right)[\text{NO}]^2[\text{O}_2]
\]
2. The rearrangement of Methy Isonitrile has been extensively studied:

\[ \text{CH}_3\text{-NC}(g) \rightarrow \text{CH}_3\text{-CN}(g) \]

Kinetic data at two different temperatures is plotted below.

At 189.7°C

\[ y = -0.0015x - 0.0002 \]

At 251.2°C

\[ y = -0.1898x - 6\times 10^{-5} \]

Determine the Activation Energy (\(E_a\)) for this reaction. (Space is provided on the next pg.)
Arrhenius Law:

\[
\ln k = - \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) + \ln A
\]

\[k_1 = 0.0015 \text{ min}^{-1} \quad \text{at} \ T_1 = 189.7 + 273.15 = 462.8 \text{ K}\]

\[k_2 = 0.1898 \text{ min}^{-1} \quad \text{at} \ T_2 = 251.2 + 273.15 = 524.3 \text{ K}\]

By the Arrhenius Law:

\[
\ln \left( \frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

or

\[
\ln \left( \frac{0.1898}{0.0015} \right) = - \frac{E_a}{(8.314 \text{ Joule/K mol})} \left( \frac{1}{524.3 \text{K}} - \frac{1}{462.8 \text{K}} \right)
\]

or

\[E_a = 159 \text{ kJ/mol}\]

3. The Autoionization Constant for Water, \(K_w\), depends on temperature:

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(K_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(1.15 \times 10^{-15})</td>
</tr>
<tr>
<td>25</td>
<td>(1.00 \times 10^{-14})</td>
</tr>
<tr>
<td>100</td>
<td>(4.90 \times 10^{-13})</td>
</tr>
</tbody>
</table>

a) What is the [H\(^+\)] in pure Water at 100°C? Recall, the Autoionization reaction is:

\[
\text{H}_2\text{O} \quad \underset{\text{H}^+(aq) + \text{OH}^-(aq)}{\xrightarrow{\text{K}_w}} \]

\[
K_w = [\text{H}^+] [\text{OH}^-]
\]

or \(4.90 \times 10^{-13} = x^2\)

\[[\text{H}^+] = x = 7 \times 10^{-7} \text{ M}\]

\[
\text{pH} = -\log(7 \times 10^{-7}) = 6.15
\]

b) Is the Autoionization of Water Endothermic or Exothermic? Explain. (Hint: Think LeChatelier.)

As T increases, \(K_w\) increases, suggesting the reaction is Endothermic.
4. Hydrogen Sulfide decomposes according to:

\[ 2 \text{H}_2\text{S(g)} \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g) \]

at 700°C. \( K_c = 9.30 \times 10^{-8} \) for this reaction, at this temperature. If we start with an initial concentration of Hydrogen Sulfide of 0.15M, what is the concentration of the products when equilibrium is established?

<table>
<thead>
<tr>
<th></th>
<th>2 H₂S</th>
<th>2 H₂</th>
<th>S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.15 M</td>
<td>0 M</td>
<td>0 M</td>
</tr>
<tr>
<td>C</td>
<td>-2x M</td>
<td>+2x M</td>
<td>+x M</td>
</tr>
<tr>
<td>E</td>
<td>0.15 - 2x</td>
<td>2x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_c = [\text{H}_2]^2 [\text{S}_2] / [\text{H}_2\text{S}]^2 \]

or \( 9.30 \times 10^{-8} = (2x)^2 (x) / (0.15 - 2x)^2 \sim (2x)^2 (x) / (0.15)^2 \)

\[ x = 8.06 \times 10^{-4} \text{M} \]

\[ [\text{H}_2] = 2x = 2 (0.000806 \text{ M}) = 0.0016 \text{ M} \]

\[ [\text{S}_2] = x = 0.0008 \text{ M} \]

5. The production of Ammonia (NH₃) is industrially important because this chemical is a feedstock for Nitrates used in manufacturing fertilizers and munitions. This reaction is Exothermic:

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

In order for the forward reaction to proceed sufficiently rapidly, fairly high temperatures are required. However, this is problematic. Briefly discuss why this is problematic.

Because the reaction is exothermic, raising the temperature will cause the equilibrium to shift left and thereby will reduce the production of NH₃. However, if you lower the temperature to alleviate this problem, you slow the reaction to the point where no NH₃ is produced in a reasonable amount of time.
Useful Information

Constants

\[ N_A = 6.022045 \times 10^{23} \text{ entities/mole} \]

\[ k_B = 1.380662 \times 10^{-23} \text{ J/K} \]

\[ c = 2.99792458 \times 10^8 \text{ m/sec} \]

\[ h = 6.626176 \times 10^{-34} \text{ J sec} \]

\[ R = 8.314 \text{ J/K mol} \]

\[ = 0.08206 \text{ L atm/K mol} \]

1 amu = 1.6605 \times 10^{-24} \text{ g} 

\[ K_w = 10^{-14} \text{ at 25^oC} \]
Periodic Table of the Elements

Main Group Representative Elements

<table>
<thead>
<tr>
<th>Main Group</th>
<th>Representative Elements</th>
<th>Main Group</th>
<th>Representative Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
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<td>8A</td>
<td>He</td>
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</tr>
<tr>
<td>18</td>
<td>Ar</td>
<td></td>
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</tr>
</tbody>
</table>

Transition metals

Metals

Metalloids

Nonmetals

Lanthanide series

Actinide series

*The labels on top (1A, 2A, etc.) are common American usage. The labels below these (1, 2, etc.) are those recommended by the International Union of Pure and Applied Chemistry (IUPAC).

The names and symbols for elements 113 and above have not yet been decided.

Atomic weights in brackets are the names of the longest-lived or most important isotope of radioactive elements.

Further information is available at http://www.webelements.com

** Discovered in 2010, element 117 is currently under review by IUPAC.