L'antipasto

Chemical Kinetics

1. Kinetic data for the following reaction was determined experimentally.
   \[2X + Y \rightarrow 3Z\]

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial Concentration (mol/L) [X]</th>
<th>Initial Concentration (mol/L) [Y]</th>
<th>Initial Rate of Reaction (mol/L•s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>0.10</td>
<td>(6.4 \times 10^2)</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>0.20</td>
<td>(2.6 \times 10^3)</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.20</td>
<td>(5.2 \times 10^3)</td>
</tr>
</tbody>
</table>

a. Determine the rate law for the reaction. (5 pt.)

b. Write the expression for the rate constant. (2 pt.)

c. What is the reaction order with respect to each reactant and the overall order? (3 pt.)
2. In basic solution, \((\text{CH}_3\text{)}_3\text{CCl}\) reacts according to the equation

\[
(\text{CH}_3\text{)}_3\text{CCl} + \text{OH}^- \rightarrow (\text{CH}_3\text{)}_3\text{COH} + \text{Cl}^-
\]

The accepted mechanism for the reaction is

\[
(\text{CH}_3\text{)}_3\text{CCl} \rightarrow (\text{CH}_3\text{)}_3\text{C}^+ + \text{Cl}^- \quad \text{(slow)}
\]

\[
(\text{CH}_3\text{)}_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3\text{)}_3\text{COH} \quad \text{(fast)}
\]

What is the rate law expression for the reaction? (5 pt.)

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3. For the following reaction between gases at equilibrium, determine the effect on the equilibrium (circle one of the following: shift left, no change, shift right) when the following changes take place. (10 pt)

\[
(\text{CH}_3\text{)}_2\text{CHOH}(g) \rightleftharpoons (\text{CH}_3\text{)}_2\text{CO}(g) + \text{H}_2(g) \quad \Delta H = +57.3 \text{ kJ}
\]

a. Increase the temperature

shift left

no change

shift right

b. Increase the volume

shift left

no change

shift right

c. Increase the pressure

shift left

no change

shift right

d. \(\text{H}_2(g)\) is added

shift left

no change

shift right

e. Add a catalyst

shift left

no change

shift right

---

*Il primo*

Equilibrium
Il contorno

Acids and Bases

4. Circle the one in each pair below that would be a stronger acid. (5 pt.)
   
a. HNO$_3$    HNO$_2$

b. HClO$_2$    HBrO$_2$

c. PH$_3$    H$_2$S

d. PH$_3$    NH$_3$

e. gallic acid, $K_a = 4.57 \times 10^{-3}$    formic acid, $K_a = 1.8 \times 10^{-4}$

5. Indicate if the following compounds would be acidic, basic, or amphoteric. (4 pt.)
   
a. Cl$_2$O$_7$    acidic    basic    amphoteric

b. Na$_2$O    acidic    basic    amphoteric

c. Al$_2$O$_3$    acidic    basic    amphoteric

d. CO$_2$    acidic    basic    amphoteric

6. In the reaction below, label the acid (A), the base (B), the conjugate acid (CA), the conjugate base (CB). (4 pt.)

   \[
   \text{NO}_2^- + \text{HClO}_4 \rightarrow \text{HNO}_2 + \text{ClO}_4^- 
   \]

7. Indicate in the example below which is the Lewis acid (LA) and which is the Lewis Base (LB). (2 pt.)

   \[
   \text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^- 
   \]
Aqueous Equilibrium

8. Of the following six (a-f) aqueous equilibrium problems, attempt to solve four (4), and only four. (9 pt. each, total of 36 pt.)

a. Calculate the pH of a 0.020 M carbonic acid solution, H$_2$CO$_3$, that has the stepwise dissociation constants of $K_{a1} = 4.3 \times 10^{-7}$, and $K_{a2} = 5.6 \times 10^{-11}$.

b. Aniline is an industrially important amine used in making dyes with $K_b$ of $4.3 \times 10^{-10}$ at 25°C. Determine the pH of an 0.050 M solution of aniline.
c. What is the pH of a 0.100 M KBrO solution if the $K_a$ of hypobromous acid, HBrO, is $2.0 \times 10^{-9}$?

d. Determine the pH of a buffer solution prepared by dissolving 0.75 mol of NH$_3$ and 0.25 mol of NH$_4$Cl in a liter of solution. $K_b = 1.8 \times 10^{-5}$ for NH$_3$. 
e. What is the silver ion concentration for a saturated solution of $\text{Ag}_2\text{CO}_3$ if the $K_{sp}$ for $\text{Ag}_2\text{CO}_3$ is $8.4\times10^{-12}$?

f. What is the molar solubility of $\text{CaF}_2$ in 0.10 M NaF solution at 25°C? The $K_{sp}$ for $\text{CaF}_2$ is $1.5\times10^{-10}$. 
Il dolce

Thermodynamics and Electrochemistry.

9. Given the following table of thermodynamic data,

<table>
<thead>
<tr>
<th>substance</th>
<th>$\Delta H^\circ_f$</th>
<th>$S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_2$(g)</td>
<td>62.25 kJ/mol</td>
<td>260.57 J/mol·K</td>
</tr>
<tr>
<td>I$_2$(s)</td>
<td>0</td>
<td>116.73</td>
</tr>
</tbody>
</table>

Determine the normal sublimation point (in °C) of iodine. (6 pt.)

10. Circle the molecule that should have the highest gas-phase absolute entropy, $S^\circ$. (3 pt.)

a. H$_2$  

b. C$_6$H$_6$  

c. HF  

d. CH$_4$  

e. C$_2$H$_6$  

f. H$_2$O

11. Determine if the change in entropy is negative or positive in the following reactions. (2 pt.)

a. BaF$_2$(s)  $\rightarrow$  Ba$^{2+}$(aq)  +  2F$^-$(aq)  

b. 2Hg(l)  +  O$_2$(g)  $\rightarrow$  2HgO(s)
12. Given the following two half-reactions

\[
\begin{align*}
\text{Cd}^{2+}(aq) + 2e^- & \rightarrow \text{Cd}(s) \quad E^\circ = -0.40 \text{ V} \\
\text{Zr}^{4+}(aq) + 4e^- & \rightarrow \text{Zr}(s) \quad E^\circ = -1.53 \text{ V}
\end{align*}
\]

Write the \textit{balanced equation} for the reaction that is \textit{spontaneous} and give the \textit{E}^\circ \textit{ of the cell}. (6 pt.)

13. \text{$E^\circ$ for the following redox reaction is $-0.029$ V:}

\[
\text{Fe}^{3+}(aq) + \text{Ag}(s) \rightarrow \text{Fe}^{2+}(aq) + \text{Ag}^+(aq)
\]

a. Calculate $\Delta G^\circ$ for the reaction. (3 pt.)

b. Calculate the equilibrium constant, K, for the reaction. (4 pt.)