Final Exam Review Key
Evaluation Link: https://docs.google.com/forms/d/13tjHRV5EHqR8KFdSJq3ufRJF9ryO1SYz6XkZQUdJj-0/edit?ts=607356c3

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UCI GCPT FALL 2021

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GCPT involves
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- EARN 2 GRADED SCIENCE UNITS
- APPLICATIONS DUE WEEK 10

- Contact uciogchmtutoring@gmail.com for more information
Kinetics

1. Consider the three-step mechanism for a reaction.

\[
\begin{align*}
\text{Cl}_2(g) & \xrightleftharpoons{k_1} 2\text{Cl}(g) \\
\text{Cl}(g) + \text{CHCl}_3(g) & \xrightarrow{k_2} \text{HCl}(g) + \text{CICH}_2(g) \\
\text{Cl}(g) + \text{Cl}_2(g) & \xrightarrow{k_3} \text{CCl}_4(g)
\end{align*}
\]

Fast

\[\text{Slow}\]

\[\text{Fast}\]

\(\text{(1.)rxn: } \text{CHCl}_3(g) + \text{Cl}_2(g) \rightarrow \text{HCl}(g) + \text{CCl}_4(g) \quad \text{rate} = k_3[\text{CHCl}_3][\text{Cl}_2]^2\]

Identify the intermediates in the mechanism and determine the predicted rate law.

\[\text{made and used in rxn: } \text{CCl}_4(g) + \text{Cl}(g)\]

\[\text{(2.)Slow(rate determining): } \]

\[\text{rate} = k_3[\text{CHCl}_3][\text{Cl}_2]\]

\[\text{(3.) switch Cl for Cl}_2\]

\[\text{rate} = k_3[\text{Cl}_2]^2 = k_4[\text{Cl}_2]^2\]

\[\text{(4.) } \text{rate} = k_3\left(\frac{k_4}{k_2}\right)^{1/2}[\text{CHCl}_3][\text{Cl}_2]^{1/2}\]

\[\text{Equilibrium} \quad \frac{\text{rate}}{k}\]

2. Coal can be used to generate hydrogen gas (a potential fuel) by the endothermic reaction:

\[\text{C(s) + H}_2\text{O(g) \rightarrow CO(g) + H}_2\text{(g)}\]

Heat\(\uparrow\)

If this reaction mixture is at equilibrium, predict whether each disturbance will result in the formation of additional hydrogen gas, the formation of less hydrogen gas, or have no effect on the quantity of hydrogen gas.

a. adding C to the mixture: no effect, solids do not contribute to equilibrium
b. adding H\(_2\)O to the reaction mixture: shift right, \(\uparrow\text{H}_2\) formation
c. raising the temperature of the reaction mixture: shift right, \(\uparrow\text{H}_2\) formation (endothermic reaction)
d. raising the volume of the reaction mixture: shift right, \(\uparrow\text{H}_2\) formation

\(\uparrow\text{volume}, \downarrow\text{pressure}, \text{shifts to side with more mols to compensate for pressure loss}\)
e. adding a catalyst to the reaction mixture: no effect, catalysts influence rate not outcome
3. Determine the percent ionization of a 0.125 M HCN solution. For HCN, \( K_a = 4.9 \times 10^{-10} \).

\[
HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq), \quad K_a = 4.9 \times 10^{-10}
\]

\[
i. \quad 0.125 \text{ M} \quad \phi \quad \phi \quad \% \text{ion} = \frac{[H_3O^+]_{eq}}{[HCN]_i} \times 100\%
\]

\[
c. \quad -x \quad +x \quad +x
\]

\[
e. \quad 0.125 - x^2 \quad x \quad x
\]

\[\text{since } K_a \ll 1, \text{ use } x \text{ is small approximation.}\]

\[K_a = \frac{[CN^-][H_3O^+]}{[HCN]}\]

\[
4.9 \times 10^{-10} \times \frac{x(x)}{0.125} \quad \checkmark \quad \frac{x}{[HCN]_c} \times 100\% = \frac{7.83 \times 10^{-6}}{0.125} \times 100\% = 6.26 \times 10^{-3}\%
\]

\[x^2 = 6.125 \times 10^{-11}\]

\[x = [H_3O^+] = 7.83 \times 10^{-6} \text{ M } \square\]

4. Find the pH of 0.175 M NaCN solution. For HCN, \( K_a = 4.9 \times 10^{-10} \).

\[
\text{NaCN} \rightarrow \text{Na}^+ + \text{CN}^- (aq)
\]

\[
0.175 \text{ M}
\]

\[
a. \quad 5.03
\]

\[
b. \quad 2.31
\]

\[
c. \quad 8.97
\]

\[
11.28
\]

\[
i. \quad 0.175 \text{ M} \quad \phi \quad \phi \quad x = 2.0 \times 10^{-5}
\]

\[
c. \quad -x \quad +x \quad +x
\]

\[
e. \quad 0.175 - x^2 \quad x \quad x
\]

\[K_b = \frac{[HCN]_{eq}[OH^-]_{eq}}{[CN^-]_{eq}}\]

\[
2.0 \times 10^{-5} \times \frac{x(x)}{0.175} \quad \checkmark \quad \text{can also do in acid w/o } \text{ Kb}.
\]

\[\text{pH} = 14 - \text{pOH}\]

\[= 14 - (-\log(1.89 \times 10^{-3}))\]

\[= 11.28\]

\[x^2 = 3.57 \times 10^{-6}\]

\[x = [OH^-] = 1.89 \times 10^{-3} \text{ M } \checkmark \quad \text{check x approx}\]
Aqueous Solutions

5. What mass of sodium benzoate should you add to 150.0 mL of a 0.15 M benzoic acid solution to obtain a buffer with a pH of 4.25? (Assume no volume change). The $K_a$ of benzoic acid is 6.3 x 10^{-5}.

\[ \text{pH} = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

\[ 4.25 = -\log(6.3 \times 10^{-5}) + \log \left( \frac{[A^-]}{0.15} \right) \]

\[ \log \left( \frac{[A^-]}{0.15} \right) = 0.049 \]

\[ 10 \cdot 0.049 = 0.49 \]

\[ [A^-] = (0.15) \cdot 10^{0.049} = 0.168 \text{ M} \]

Molarity = \( \frac{\text{mol}}{L} \)

\[ 0.168 \text{ M} = \frac{x \text{ mol}}{0.15 \text{ L}} \]

\[ x = 0.0252 \text{ mol NaC}_7\text{H}_5\text{O}_2 \]

\[ \text{Molar mass (144.1 g/mol)} \]

\[ \text{NaC}_7\text{H}_5\text{O}_2 \]

\[ = 3.63 \text{ grams needed} \]

Solubility

6. Use the given molar solubility of MgF$_2$ (2.65 x 10^{-4} M) in pure water to calculate its $K_{sp}$.

\[ \text{molar solubility of salt that will completely dissolve in 1 L of solution} \]

\[ \text{MgF}_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq) \]

\[ K_{sp} = [F^-]^2[Mg^{2+}] \]

\[ = (2s)^2(s) = 4s^3 \]

\[ K_{sp} = 4(2.65 \times 10^{-4})^3 \]

\[ K_{sp} = 7.14 \times 10^{-11} \]
Redox Reactions

1. Assign oxidation numbers to all the elements in the following compounds and ion:
   a. \( Na_2O \)
   b. \( HNO_2 \)
   c. \( Cr_2O_7^{2-} \)

2. Write a balanced ionic equation to represent the oxidation of iodide ion (\( I^- \)) by permanganate ion (\( MnO_4^- \)) in basic solution to yield molecular iodine (\( I_2 \)) and manganese(IV) oxide (\( MnO_2 \)).
3. Write the cell notation for a voltaic cell with the following half-reactions.

\[ \text{Ni(s)} \rightarrow \text{Ni}^{2+} \text{ (aq)} + 2e^- \]
\[ \text{Pb}^{2+} \text{ (aq)} + 2e^- \rightarrow \text{Pb(s)} \]
4. Consider the reaction

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

Does the reaction go spontaneously in the direction indicated, under standard conditions?

Calculating \( E^0 \) cell

5. a. Consider a galvanic cell based on the reaction

\[ \text{Al}^{3+}(aq) + \text{Mg}(s) \rightarrow \text{Al}(s) + \text{Mg}^{2+}(aq) \]

The half reaction are

\[ \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \quad E^o = -1.66 \text{ V} \]

\[ \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg} \quad E^o = -2.37 \text{ V} \]
Give the balanced cell reaction, and calculate $E^o$ for the cell.

b. A galvanic cell is based on the reaction

$$MnO_4^- (aq) + H^+ (aq) + ClO_3^- (aq) \rightarrow ClO_4^- (aq) + Mn^{2+} (aq) + H_2O (l)$$

The half-reactions are

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \quad E^o = 1.51 \text{ V}$$

$$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O \quad E^o = 1.19 \text{ V}$$
6. Using standard electrode potentials, calculate the standard free-energy change at 25°C for the reaction

\[
\text{Zn}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)
\]
E°_cell and Equilibrium

1. Use the tabulated electrode potentials to calculate the K for the oxidation of the iron by H^+ (at 25°C).

\[
2 \text{Fe}(s) + 6 \text{H}^+(aq) \rightarrow 2 \text{Fe}^{3+}(aq) + 3\text{H}_2(g)
\]

2Fe (s) → 2Fe^{3+} (aq) OXIDATION (ANODE)
Tabulated electrode potential:
Fe (s) → Fe^{3+} + 3e^-

Electron transfer:
2Fe (s) → 2Fe^{3+} (aq) + 6e^- \quad E°_\text{cell} = -0.036V

6H^+ (aq) → 3H_2 (g) REDUCTION (CATHODE)
Tabulated electrode potential:
2H^+ (aq) + 2e^- → H_2 (g)

Electron transfer (Multiply by 3 to match electrons) \quad E°_\text{cell} = 0.00V
6H^+ + 6e^- → 3H_2 (g)

E°_\text{cell} = E_\text{cathode} - E_\text{anode}
E°_\text{cell} = (0.00V) - (-0.036V)
E°_cell = +0.036 V

Nernst Equation - E_{cell} under Nonstandard Conditions

2. A galvanic cell is made from a solution of Cu^{2+} (aq) with a Cu (s) electrode and a separate solution of Zn^{2+} (aq) with a Zn (s) electrode. The two half-cells are linked by a salt bridge and the cell is run at 25°C.

   a) Calculate E_{cell} when [Cu^{2+}] = 1.0 M and [Zn^{2+}] = 0.10 M

   Zn (s) + Cu^{2+} (aq) ←→ Zn^{2+} (aq) + Cu (s)
   Cathode: Cu^{2+} (aq) + 2e^- → Cu (s)  E°_cathode = 0.34 V
   Anode: Zn (s) → Zn^{2+} (aq) + 2e^-  E°_anode = -0.76 V

   E°_cell = E°_cathode - E°_anode
   E°_cell = (0.34 V) - (-0.76 V)
   E°_cell = 1.10 V

   E°_cell = 1.10 V, so we can calculate Q now. These are non-standard conditions:
   Q = [Zn^{2+}]/[Cu^{2+}] = 0.10/1.0 = 0.10

   Thus,
   E_{cell} = E°_cell - (RT/nF)(lnQ)
   We know E_{cell} = E°_cell - (RT/nF)ln(Q) = 1.10 V
   E_{cell} = 1.10 - \frac{(8.314)(298.15)}{(2)(96,485)}ln(0.10) = 1.13 V

3. Determine the cell potential for an electrochemical cell based on the following two half-reactions:
   Oxidation: Cu (s) → Cu^{2+} (aq, 0.010 M) + 2e^{-}
   Reduction: MnO_4^- (aq, 2.0M) + 4H^+ (aq, 1.0M) + 3e^- → MnO_2 (s) + 2H_2O (l)

   [MnO_4^-] = 2.0 M
   [H^+] = 1.0 M
   [Cu^{2+}] = 0.010 M
Determine $E_{\text{cell}}$.

$3 \ [\text{Cu(s)} \rightarrow \text{Cu}^{3+}\text{(aq)} + 2e^{-}] \quad E^\circ = 0.34 \text{ V}$
$2 \ [\text{MnO}_4^-\text{(aq)} + 4\text{H}^+\text{(aq)} + 3e^- \rightarrow \text{MnO}_2\text{(s)} + 2\text{H}_2\text{O(l)}] \quad E^\circ = 1.68 \text{ V}$

$3\text{Cu(s)} + 2\text{MnO}_4^-\text{(aq)} + 8\text{H}^+\text{(aq)} \rightarrow 3\text{Cu}^{2+}\text{(aq)} + 2\text{MnO}_2\text{(s)} + 4\text{H}_2\text{O(l)}$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
$E^\circ_{\text{cell}} = (1.68 \text{ V}) - (0.34 \text{ V})$
$E^\circ_{\text{cell}} = 1.34 \text{ V}$

$E_{\text{cell}} = 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log(Q)$
$E_{\text{cell}} = 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log\left(\frac{(0.010)^3}{(2.0)^2(1.0)^8}\right)$
$E_{\text{cell}} = 1.34 \text{ V} - (-0.065 \text{ V})$
$E_{\text{cell}} = 1.41 \text{ V}$

4. A redox reaction has an $E^\circ_{\text{cell}} = -0.56\text{V}$. What can you conclude about the equilibrium constant (K) for the reaction?

   a) $K < 1$
   b) $K > 1$
   c) $K = 0$
   d) Nothing can be concluded about K from $E^\circ_{\text{cell}}$

For nonspontaneous reactions, $\Delta G^\circ$ is positive ($>0$), $E^\circ_{\text{cell}}$ is negative ($<0$), and therefore, $K < 1$.

Voltage Decline

5. Suppose that we make a zinc-iron cell at 25°C that is initially at standard conditions.

$\text{Zn (s)} + \text{Fe}^{2+} (\text{aq}) \leftrightarrow \text{Zn}^{2+} (\text{aq}) + \text{Fe (s)}$

Calculate the cell potential:
   (a) before discharge

Oxidation: $\text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2e^- \quad E^\circ = -0.76 \text{ V}$
Reduction: $\text{Fe}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Fe (s)} \quad E^\circ = -0.41 \text{ V}$
\[ E^\circ_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]

\[ E^\circ_{\text{cell}} = (-0.41 \text{ V}) - (-0.76 \text{ V}) \]

\[ E^\circ_{\text{cell}} = 0.35 \text{ V} \]

(b) when 99% of the Fe\(^{2+}\) ions have been reduced

At standard conditions, both concentrations of Fe\(^{2+}\) (aq) and Zn\(^{2+}\) (aq) are 1.00 M. When 99% of the Fe\(^{2+}\) is reduced → [Fe\(^{2+}\)] = 0.01 M and [Zn\(^{2+}\)] = 1.99 M.

\[ Q = [\text{Zn}^{2+}]/[\text{Fe}^{2+}] \]

\[ Q = 1.99 \text{ M/0.01 M} \]

\[ Q = 199 \]

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - ((0.0257/n)\times \ln Q) \]

\[ E_{\text{cell}} = 0.35 \text{ V} - ((0.0257/2) \times \ln(199)) \]

\[ E_{\text{cell}} = 0.282 \text{ V} \]

Clearly, the voltage decreases from 0.35V to 0.282V.

Plating

6. Copper can be electroplated at the cathode of an electrolytic cell by the half-reaction:

\[ \text{Cu}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cu} (\text{s}) \]

How much time does it take for 325 mg of copper to be plated at a current of 5.6A?

\[
325 \text{ mg Cu} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Cu}}{63.546 \text{ g}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{96485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{5.6 \text{ C}} = 1.8 \times 10^2 \text{ s}
\]