General Chemistry Peer Tutoring
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Chem 1C
Professor Potma
https://sites.uci.edu/gcptutoring/

Final Review Answer Key

Topics Covered

Kinetics

- Average reaction rate
- Determining rate law from experimental data and reaction mechanism
- Integrated rate laws and half-life

Equilibrium

- Calculating equilibrium concentrations: equilibrium constant (K_c), reaction quotient (Q_c)
- Le Chatelier's principle
- Gibbs free energy

Acids and Bases

- Definition of acids and bases (Arrhenius, Bronsted, Lewis)
- Strength of acids/bases: ionization constants (K_a, K_b) and percent ionization
- Polyprotic solvents

Aqueous Ionic Equilibrium

- Common ion effect, Henderson Hasselbach equation
- Buffer capacity: pH percent change, buffer range
- Solubility, equilibrium constant K_{sp}
- Complex ion formation

Electrochemistry

- Calculating oxidation states
- Balancing redox reactions (basic and acidic)
- Galvanic cells
- Spontaneity of redox reactions

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Practice Questions

1. Iodide ion is oxidized in acidic solution to triiodide ion, I_3^- , by hydrogen peroxide.

   H_2O_2 (aq) + $3I^-$ (aq) + $2H^+$ (aq) → I_3^- (aq) + $2H_2O$ (l)

   A series of four experiments was run at different concentrations, and the initial rates of I_3^- formation were determined. (Darrell 9th Ed. 13.4)

	Initial Concentrations (mol/L)			Initial Rate
	H_2O_2	I^-	H^+	[mol/(L*s)]
Trial 1	0.010	0.010	0.00050	1.15×10^{-6}
Trial 2	0.020	0.010	0.00050	2.30×10^{-6}
Trial 3	0.010	0.020	0.00050	2.30×10^{-6}
Trial 4	0.010	0.010	0.00100	1.15×10^{-6}

   a. From these data, obtain the reaction orders with respect to H_2O_2, I^-, and H^+.

$$\text{Rate} = k[H_2O_2]^m[I^-]^n[H^+]^p$$

For H_2O_2, compare T_1/T_2

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{[H_2O_2]_2}{[H_2O_2]_1}\right)^m$$

$$\frac{2.30\times10^{-6}}{1.15\times10^{-6}} = \left(\frac{0.020}{0.010}\right)^m$$

$$2 = (2)^n$$

$n = 1$

For I^-, compare T_1/T_3

$$2 = (2)^n$$

$n = 1$

For H^+, compare T_1/T_4

$$1 = (2)^n$$

$n = 0$

The reaction orders with respect to H_2O_2, I^-, and H^+, are **1, 1, and 0**, respectively. Note that the orders are *not* related to the coefficients of the overall equation.

b. Find the rate constant.

You calculate the rate constant by substituting values from any of the experiments into the rate law. Using Experiment 1, you obtain

$$\frac{1.15 \times 10^{-6}\ \text{mol}}{\text{L} \times \text{s}} = k \times \left(\frac{0.010\ \text{mol}}{\text{L}}\right)^{1} \times \left(\frac{0.010\ \text{mol}}{\text{L}}\right)^{1} \times \left(\frac{0.0050\ \text{mol}}{\text{L}}\right)^{0}$$

$$k = \frac{1.2 \times 10^{-2}\ \text{L}}{\text{mol} \times \text{s}}$$

2. The decomposition of N_2O_5 to NO_2 and O_2 is first order, with a rate constant of 4.80 × 10^{-4} /s. (Darrell 9th Ed. 13.5)

a. If the initial concentration is 1.65×10^{-2} mol/L, what is the concentration after 825 s?

In this case, you need to use the equation relating concentration to time for a first-order reaction, which is

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{[N_2O_5]_t}{1.65 \times 10^{-2}\ \text{mol/L}} = \frac{-4.80 \times 10^{-4}}{\text{s}} \times 825\ \text{s}$$

$$\ln \frac{[N_2O_5]_t}{1.65 \times 10^{-2}\ \text{mol/L}} = -0.396$$

$$\frac{[N_2O_5]_t}{1.65 \times 10^{-2}\ \text{mol/L}} = 0.673$$

$$[N_2O_5]_t = 0.0111\ \text{mol/L}$$

b. How long would it take for the concentration of N_2O_5 to decrease to 1.00×10^{-2} mol/L from its initial value, given in a?

$$\ln \frac{1.00 \times 10^{-2}\ \text{mol/L}}{1.65 \times 10^{-2}\ \text{mol/L}} = \frac{-4.80 \times 10^{-4}}{\text{s}} \times t$$

$$-0.501 = \frac{-4.80 \times 10^{-4}}{\text{s}} \times t$$

$$t = 1.04 \times 10^{3}\ \text{s}$$

c. How long would it take for the concentration of N_2O_5 to decrease to 10.0% of its initial value?

$$\ln(0.10) = -4.80 \times 10^{-4} \times t$$

$$t = 4797\ \text{s}$$

3. Nitrogen monoxide can be reduced with hydrogen gas to give nitrogen and water vapor.

   $2NO\,(g) + 2H_2\,(g) \rightarrow N_2\,(g) + 2H_2O\,(g)$ (overall equation)

   A proposed mechanism is

   $2NO \rightleftharpoons N_2O_2$ (fast, equilibrium)
   $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
   $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

   What rate law is predicted by this mechanism? (Darrell 9th Ed. 13.12)

   Examining the reaction mechanism, you can see that it has an initial fast, equilibrium step, followed by a slow step. You write the rate equation for the rate-determining (slow) step, just as in the previous example. In this case, however, the equation contains a species, N_2O_2, that does not appear in the overall equation for the reaction. You need to eliminate it from the final form of the rate law. Note that the first step is fast and reaches equilibrium. You use this fact to write an expression for $[N_2O_2]$. Then you substitute this expression for $[N_2O_2]$ into the rate equation.

$$\text{Rate} = k_2[N_2O_2][H_2]$$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

$$\text{Rate} = k[NO]^2[H_2]$$

4. A 50.0-L reaction vessel contains 1.00 mol N_2, 3.00 mol H_2, and 0.500 mol NH_3. Will more ammonia, NH_3, be formed or will it dissociate when the mixture goes to equilibrium at 400°C? The equation is:
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   K_c is 0.500 at 400°C. (Darrell 9th Ed. 14.5)

   Answer: The composition of the gas has been given in terms of moles. You convert these to molar concentrations by dividing by the volume (50.0 L). This gives 0.0200 M N_2, 0.0600 M H_2, and 0.0100 M NH_3. Substituting these concentrations into the Q_c gives:

   $$Q_c = \frac{[NH3]^2}{[N2][H2]^3} = \frac{(0.0100)^2}{(0.0200)(0.0600)^3} = 23.1$$

   Because $Q_c = 23.1$ is greater than $K_c = 0.500$, the reaction will go to the left as it approaches equilibrium. Therefore, ammonia will dissociate.

5. Consider each of the following equilibria, which are disturbed as indicated. Predict the direction of reaction. (Darrell 9th Ed. 14.12-14.14)

   a. Increasing the pressure of the following reaction:
      $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

      An increase in pressure will cause the reaction to shift towards the side with fewer moles of gas. Reaction will shift **towards the reactants**.

   b. Increasing the concentration of hydrogen:
      $2Fe(s) + 3H_2O(g) \rightleftharpoons Fe_2O_3(s) + 3H_2(g)$

      The reaction will shift **towards the reactants** to try to create more products to offset the addition of H_2.

   c. Increasing the temperature of the following endothermic reaction:
      $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$.

      Endothermic means heat acts as a reactant. Increasing temperature shifts reaction to the right, **towards the products**.

6. Ascorbic acid (vitamin C) is a diprotic acid, $H_2C_6H_6O_6$. The acid ionization constants are $K_{a1} = 7.9 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$. (Darrell 9th Ed. 16.4)

   a. What is the pH of a 0.10 M solution?

$H_2Asc\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HAsc^-\ (aq)$ $\quad K_{a1} = 7.9 \times 10^{-5}$

$HAsc^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Asc^{2-}\ (aq)$ $\quad K_{a2} = 1.6 \times 10^{-12}$

	$H_2Asc\ (aq)$	$+\ H_2O\ (l)$	$\rightleftharpoons H_3O^+\ (aq)$	$+\ HAsc^-\ (aq)$
I	0.10	–	0	0
C	$-x$	–	$+x$	$+x$
E	$0.10-x$	–	x	x

$$\frac{[H_3O^+][HAsc^-]}{[H_2Asc]} = K_{a1}$$

$$\frac{x^2}{0.10-\cancel{x}} = 7.9 \times 10^{-5}$$

$$x = 0.0028 \leftarrow [H_3O^+]$$

$pH = -\log[H_3O^+]$

$pH = -\log(0.0028)$

$pH = 2.55$

   b. What is the concentration of ascorbate ion, $C_6H_6O_6^{2-}$?

	$HAsc^-\ (aq)$	$+\ H_2O\ (l)$	$\rightleftharpoons H_3O^+\ (aq)$	$+\ Asc^{2-}\ (aq)$
I	0.0028	–	0.0028	0
C	$-y$	–	$+y$	$+y$
E	$0.0028-y$	–	$0.0028+y$	y

$$\frac{[H_3O^+][Asc^{2-}]}{[HAsc^-]} = K_{a2}$$

$$\frac{(0.0028\cancel{+y})(y)}{(0.0028-\cancel{y})} = 1.6 \times 10^{-12}$$

$$y = 1.6 \times 10^{-12}$$

Therefore, $[Asc^{2-}] = 1.6 \times 10^{-12}\ M$

7. Determine whether the mixing of each pair of solutions results in a buffer. (Tro 1st ed. Ch 18 #52)
   a. 75.0 mL of 0.10 M HF; 55.0 mL of 0.15 M NaF

      Yes, this will be a buffer because HF is a weak acid and F is its conjugate base. The ratio of base to acid is (0.0550 x 0.15) / (0.075 x 0.10) = 1.1, so the pH will be within 1 pH unit of the pKa (based on the Henderson-Hasselbach equation)

   b. 150.0 mL of 0.10 M HF; 135.0 mL of 0.175 M HCl

      No, this will not be a buffer because they are both acids. HF is a weak acid, and HCl is a strong acid.

   c. 165.0 mL of 0.10 M HF; 135.0 mL of 0.050 M KOH

      Yes, this will be a buffer. HF is a weak acid and KOH (strong base) will convert enough HF to its conjugate base.

	HF (aq)	OH^- (aq)	F^- (aq)	H_2O (l)
Initial (I)	0.0165	0.00675	0	-
Change (C)	-0.00675	-0.00675	+0.00675	-
Equilibrium (E)	0.01	0	0.00675	-

Conjugate base to acid ratio: $\frac{0.00675}{0.01} = 0.675$ <- The pH will be within 1 pH unit of the pKa.

   d. 125.0 mL of 0.15 M CH_3NH_2; 120.0 mL of 0.25 M CH_3NH_3Cl

      Yes, this will be a buffer because CH_3NH_2 is a weak base and CH_3NH_3Cl is its conjugate acid. The ratio of base to acid is (0.125 x 0.15) / (0.120 x 0.25) = 0.63. The pH will be within 1 pH unit fo the pKa.

   e. 105.0 mL of 0.15 M CH_3NH_2; 95.0 mL of 0.10 M HCl

      Yes, this will be a buffer. CH_3NH_2 is a weak base and HCl (strong acid) will convert CH_3NH_2 to its conjugate acid.

	CH_3NH_2 (aq)	HCl (aq)	Cl^- (aq)	$CH_3NH_3^+$ (aq)
Initial (I)	0.016	0.0095	0	0
Change (C)	-0.0095	-0.0095	+0.0095	+0.0095
Equilibrium (E)	0.0065	0	0.0095	0.0095

Conjugate base to acid ratio: $\frac{0.0065}{0.0095} = 0.68$ <- The pH will be within 1 pH unit of the pKa.

8. A solution containing potassium bromide is mixed with one containing lead acetate to form a solution that is 0.013 M in KBr and 0.0035 M in $Pb(C_2H_3O_2)_2$. Does a precipitate form in the mixed solution? (Tro 1st. Ed Ch 18 #100)

   K_{sp} of $PbBr_2 = 4.67 \times 10^{-6}$

   Calculate Q_{sp}

   $Q_{sp} = [Pb^{2+}][Br^-]^2 = [0.0035][0.013]^2 = 6.0 \times 10^{-7}$

   Note: Make sure the ion concentrations are correct. In this problem, the concentrations don't have to be changed because there's one Pb per $Pb(C_2H_3O_2)_2$ and one Br per KBr.

   $Q_{sp} < K_{sp}$, so precipitate will not form.

9. Obtain the oxidation number for the element noted in each of the following. (Ebbing 9th ed. Ch 4 #57)
   a. N in NH_2^-

      Hydrogen is +1 in covalent compounds. Add the known oxidation numbers to the equal the overall charge of the compound.
      $N + 2(+1) = -1$
      $N = -3$

   b. I in IO_3^-

      $I + 3(-2) = -1$ Oxygen is usually -2 (except in H_2O_2 where it's -1)
      $I = +5$

   c. Al in $Al(OH)_4^-$

      $Al + 4(-1) = -1$ OH has an oxidation number of -1

Al = +3

d. Cl in $HClO_4$

$(+1) + Cl + 4(-2) = 0$
Cl = +7

10. Balance the following oxidation–reduction equations. The reactions occur in acidic or basic aqueous solution, as indicated. (Ebbing 9th ed. Ch 18 #41)

a. $MnO_4^- + I^- \rightarrow MnO_2 + IO_3^-$ (basic)

Step 1: Balance the oxidation and reduction half reactions
Oxidation: $I^- + 3H_2O \rightarrow IO_3^- + 6H^+ + 6e^-$
Reduction: $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$
-> $2MnO_4^- + 8H^+ + 6e^- \rightarrow 2MnO_2 + 4H_2O$ *Reaction multiplied by 2 to get $6e^-$

Step 2: Combine the half reactions and add OH to create water (remove H^+)
$2H^+ + 2MnO_4^- + I^- \rightarrow IO_3^- + 2MnO_2 + H_2O$
$2OH^- + 2H^+ + 2MnO_4^- + I^- \rightarrow IO_3^- + 2MnO_2 + H_2O + 2OH^-$
$2H_2O + 2MnO_4^- + I^- \rightarrow IO_3^- + 2MnO_2 + H_2O + 2OH^-$
$2MnO_4^- + I^- + H_2O \rightarrow IO_3^- + 2MnO_2 + 2OH^-$

b. $Cr_2O_7^{2-} + Cl^- \rightarrow Cr^{3+} + Cl_2$ (acidic)

Step 1: Balance the oxidation and reduction half reactions
Oxidation: $2Cl^- \rightarrow Cl_2 + 2e^-$
-> $6Cl^- \rightarrow 3Cl_2 + 6e^-$ *Reaction multiplied by 3 to get $6e^-$
Reduction: $14H^+ + 6e^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

Step 2: Combine the half reactions
$14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$

c. $H_2O_2 + MnO_4^- \rightarrow O_2 + MnO_2$ (basic)

Step 1: Balance the oxidation and reduction half reactions
Oxidation: $H_2O_2 \rightarrow O_2 + 2e^- + 2H^+$
-> $3H_2O_2 \rightarrow 3O_2 + 6e^- + 6H^+$ *Reaction multiplied by 3 to get $6e^-$
Reduction: $4H^+ + 3e^- + MnO_4^- \rightarrow MnO_2 + 2H_2O$
-> $8H^+ + 6e^- + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$ *Reaction multiplied by 2

Step 2: Combine the half reactions and add OH to create water (remove H^+)

$2H^+ + 3H_2O_2 + 2MnO_4^- \rightarrow 2MnO_2 + 3O_2 + 4H_2O$

$2OH^- + 2H^+ + 3H_2O_2 + 2MnO_4^- \rightarrow 2MnO_2 + 3O_2 + 4H_2O + 2OH^-$

$2H_2O + 3H_2O_2 + 2MnO_4^- \rightarrow 2MnO_2 + 3O_2 + 4H_2O + 2OH^-$

$\mathbf{3H_2O_2 + 2MnO_4^- \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-}$

d. $Zn + NO_3^- \rightarrow Zn^{2+} + N_2$ (acidic)

Step 1: Balance the oxidation and reduction half reactions

Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

-> $5Zn \rightarrow 5Zn^{2+} + 10e^-$ *Reaction multiplied by 5 to get $10e^-$

Reduction: $2NO_3^- + 12H^+ + 10e^- + \rightarrow N_2 + 6H_2O$

Step 2: Combine the half reactions and add OH to create water (remove H^+)

$\mathbf{2NO_3^- + 12H^+ + 5Zn \rightarrow 5Zn^{2+} + N_2 + 6H_2O}$

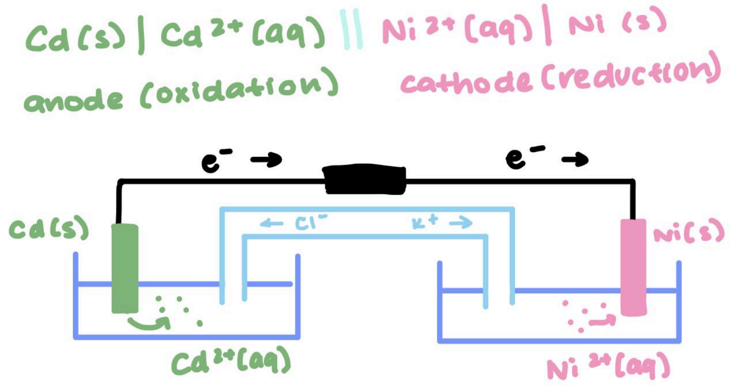
11. Consider the voltaic cell $Cd(s) \mid Cd^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$

Write the half-cell reactions and the overall cell reaction. Make a sketch of this cell and label it. Include labels showing the anode, cathode, and direction of electron flow. (Ebbing 6th ed. Ch 19 #55)

Anode: $Cd(s) \rightarrow Cd^{2+} + 2e^-$

Cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

Overall: $Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+} + Ni(s)$



Standard Reduction Potentials

Half Reaction	E°cell (V)
Ag^+ (aq) + e^- → Ag (s)	0.80
O_2 (g) + $2H_2O$ (l) + 4 e^- → 4 OH^- (aq)	0.40
Br_2 (l) + $2e^-$ → 2 Br^- (aq)	1.09
I_2 (s) + $2e^-$ → 2 I^- (aq)	0.54
Sn^{2+} (aq) + $2e^-$ → Sn (s)	– 0.14
Fe^{3+} (aq) + $3e^-$ → Fe (s)	– 0.036

12. Calculate E°cell for each balanced redox reaction and determine if the reaction is spontaneous as written. (Tro 1st ed. Ch 20 #58)

a. O_2 (g) + $2H_2O$ (l) + 4Ag (s) → $4OH^-$ (aq) + $4Ag^+$ (aq)

Separate reactions into oxidation and reduction

Reduction: O_2 (g) + $2H_2O$ (l) + $4e^-$→ $4OH^-$ (aq) 0.40 V

Oxidation: 4Ag (s) → $4Ag^+$ (aq) + $4e^-$

-> simplify to Ag (s) → Ag^+ (aq) + e^- 0.80 V

$E°_{cell} = E°_{cathode} - E°_{anode}$

$E°_{cell}$ = 0.40 V - 0.80 V = **– 0.40 V**

This reaction is nonspontaneous because $E°_{cell} < 0$

b. Br_2 (l) + $2I^-$ (aq) → $2Br^-$ (aq) + I_2 (s)

Reduction: Br_2 (l) + $2e^-$→ $2Br^-$ (aq) 1.09 V

Oxidation: $2I^-$ (aq) → I_2 (s) + $2e^-$ 0.54 V

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

E°_{cell} = 1.09 V - 0.54 V = **0.55 V**

This reaction is nonspontaneous because $E^{\circ}_{cell} > 0$

13. Use tabulated electrode potentials to calculate ΔG° for each reaction at 25°C. (Tro 1st ed. Ch 20 #62)
    a. $2Fe^{3+}$ (aq) + 3Sn (s) → 2Fe (s) + $3Sn^{2+}$ (aq)

       Reduction: $2Fe^{3+}$ (aq)) + $6e^{-} \rightarrow$ 2Fe (s) – 0.036 V

       Oxidation: 3Sn (s) → $3Sn^{2+}$ (aq) + $6e^{-}$ – 0.14 V

       $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

       E°_{cell} = -0.036 V - (- 0.014 V) = 0.104 V

       $\Delta G^{\circ}_{rxn} = -\ nFE^{\circ}_{cell}$

       ΔG°_{rxn} = – (6 mol e^{-}) (96,485 C/ mol e^{-}) (0.104 V) = **– 6.0 x 10^{4} J**

    b. Br_2 (l) + $2I^{-}$ (aq) → $2Br^{-}$ (aq) + I_2 (s)

       From # 12b: E°_{cell} = 0.55 V

       $\Delta G^{\circ}_{rxn} = -\ nFE^{\circ}_{cell}$

       ΔG°_{rxn} = – (2 mol e^{-}) (96,485 C/ mol e^{-}) (0.55 V) = **– 1.1 x 10^{5} J**

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