

CH 123 Study Problems

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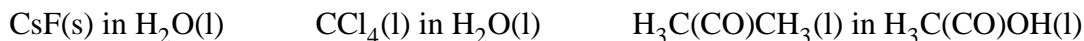
April 12, 2004

The questions in this set are examples of problems that you should be able to solve by taking the course. While they should cover the key information of the course, they are not meant to be complete or exhaustive. Review the summary discussions at the end of each chapter for descriptions of the information you are required to know. Further example problems are provided in the textbook and via the homework.

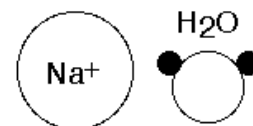
A solution key for these study problems will not be provided. You are welcome to visit me with your solutions to the problems to discuss whether they are correct.

Solutions

1. Which system below is likely to form an immiscible solution over a certain range of concentration?



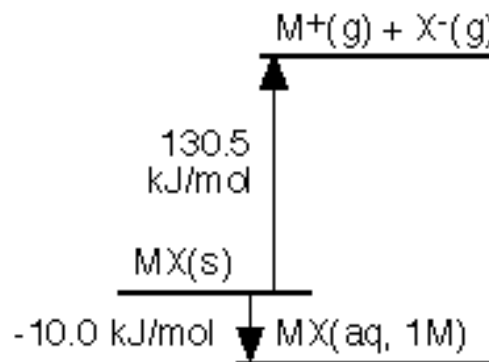
2. Show a picture that represents how water molecules might be arranged around a sodium ion to hydrate the ion. A sodium ion and water molecule are given to approximate scale.



3. A _____ is a species that acts at an oil/water interface to help dissolve oil into water.
4. A solution contains exactly 1 molal KCl in water. What is the wt% KCl in the solution? (molar masses: KCl = 74.5510 g/mol, H₂O = 18.0148 g/mol).
5. A doped semiconductor wafer is produced by dissolving 0.2500 g P in 1 kg Si. What is the concentration of P in Si in ppm?

6. Consider the two reaction enthalpies shown in the Born-Haber diagram on the right.

- a) When temperature decreases, will the solubility of MX(s) increase or decrease?
- b) Show an arrow on the diagram that corresponds to the hydration reaction.
- c) What is the value of the molar enthalpy of hydration of MX?



7. The solubility of CO₂ in water is 0.0656 M at 1.50 atm. What is the Henry's law constant for CO₂ in water?

8. Consider the following solutions.

0.10 m $\text{CaCl}_2(\text{aq})$ 0.25 m $\text{KF}(\text{aq})$ 0.20 m $\text{MgF}_2(\text{aq})$ 0.10 m $\text{NaCl}(\text{aq})$

a) Which solution will show the greatest increase in boiling temperature over pure water?

b) Which solutions will have approximately equal freezing temperatures. If they each have significantly different freezing temperatures from one another, answer NONE OF THEM.

9. The osmotic pressure of a certain aqueous solution is exactly 100 kPa at 25 °C. What is the molar concentration of the solution?

10. What is the molal concentration of a 1.00 molar solution of NaCl in water? $M_{\text{NaCl}} = 58.443$ g/mol. Assume water has a density of exactly 1 Mg/m³.

11. You are to prepare 50.0 ml of an aqueous solution of 0.155 M KCl. What mass (g) of KCl is needed? $M_{\text{KCl}} = 74.551$ g/mol

12. A stock solution of 0.155 M KCl is to be diluted to produce 10.0 ml of a solution at 0.050 M KCl concentration. What volume (ml) of the stock solution is needed?

13. A liquid solution of MgO + NiO has exactly 50 mol% MgO. What is the mass fraction of MgO? $M_{\text{MgO}} = 40.3044$ g/mol, $M_{\text{NiO}} = 74.6928$ g/mol

14. A room contains 40×10^3 moles of air. It is saturated with benzene (BZ) vapor to a concentration of 375. ppm. What mass (g) of BZ was added? $M_{\text{BZ}} = 78.11364$ g/mol, $M_{\text{air}} = 28.850$ g/mol

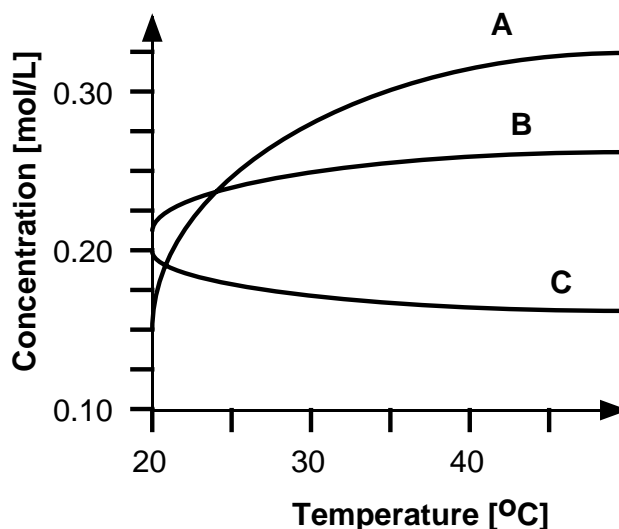
15. A pure metal contains a different element dissolved in it in the solid state. What is the resulting solid called?

16. Covalently bonded solids are most likely to dissolve in what type of liquid? a) polar, b) non-polar, c) either, or d) unable to tell.

17. A supersaturated solution will have a) one phase or b) two phases?

18. The graph on the right shows the solubility of compounds A, B, and C in water.

- For compounds A and B, is $\Delta_{soln}\bar{H}$ exothermic or endothermic?
- At 30 °C, what is the saturation concentration of A in water? Show on the graph the lines you use to read the value.
- What temperature is required to have a solubility limit of 0.25 mol/L of A?



- Explain the process of hydration. Illustrate your explanation appropriately.
- What factor(s) will affect the enthalpy of hydration of an ion? a) size of ion, b) shape of ion, c) polarity of solvent, d) shape of solvent molecule, e) charge of ion.
- Consider the following two reactions:

$$\text{KCl(s)} \rightarrow \text{K}^+(\text{g}) + \text{Cl}^-(\text{g}) \quad \Delta\bar{H}^\circ = 950 \text{ kJ/mol}$$

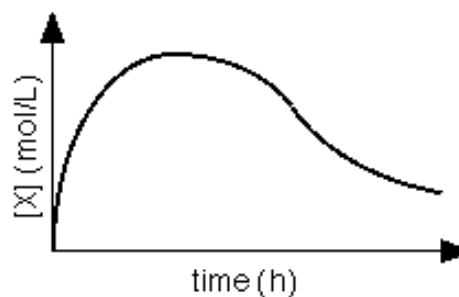
$$\text{KCl(s)} \rightarrow \text{KCl(aq, 1m)} \quad \Delta\bar{H}^\circ = 5 \text{ kJ/mol}$$
 Determine the enthalpy of hydration of KCl (kJ/mol).
- The solubility of a gas in a liquid is determined by a) Raoult's law, b) Henry's law, c) Le Chatelier's principle, d) none of these.
- The osmotic pressure of a solution of KCl(aq) at 25 °C is 7.75 atm. What is the molar concentration of KCl in the solution?
- A solution contains 0.0675 moles ethanol in 1.4325 moles water at 100 °C. What is the vapor pressure (atm) of the water in the solution under these conditions? Assume the mixture forms an ideal solution. (Hint: pure water at 1 atm boils at 100 °C)
- The freezing point depression constant of KCl in water is 3.54 °K/m. Determine the freezing point (°C) of a 0.015 m solution of KCl(aq). Assume the van't Hoff factor is 2, and water freezes at 0 °C.
- Explain the differences between a colloid and a solution.

27. Water loving colloids are a) hydrophobic or b) hydrophilic?
28. Explain how a surfactant works. Illustrate your explanation appropriately.

Kinetics

- Consider the reaction $A(g) + 3B(g) \rightarrow 2C(g)$ at constant temperature and volume. The empirical rate expression is first order in $[B]$ and inverse first order in $[A]$.
 - When the pressure of A is cut in half, by what factor does the overall rate change?
 - When $[A] = 3.0 \text{ M}$ and $[B] = 1.0 \text{ M}$, the rate is 0.15 mol/L s . What is the empirical rate constant?
 - The reaction rate of C is 108.0 mol/L h . What is the reaction rate of A?
- A first order reaction with a half life of 77.333 s is started with an initial concentration of 0.250 M . How long is required to reach a concentration of 0.025 M ?

- The curve on the right shows concentration versus time for a chemical reaction.



- Show with a \star the point on the curve that corresponds to a reaction rate of zero.
 - Draw the straight line that would be used to calculate the initial rate of the reaction.
- Based on the above curve, would you say the species X is a reactant, an intermediate, or a product in the overall reaction?
- Consider the three elemental reaction steps shown below.
 - $A + B \rightarrow C$
 - $B + C \rightleftharpoons D$ (equilibrium)
 - $D + C \rightarrow E + F$ (slow)
 - What is the overall reaction?
 - What is the overall reaction if C is an intermediate and should not appear in the final overall reaction expression?
 - Circle the empirical rate expression that agrees with the mechanism. (2)

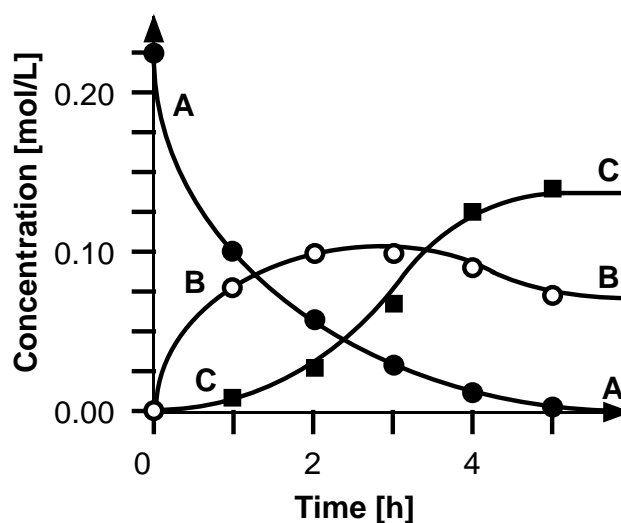
$k[A][B]$ $k[A][C]$ $k[A][C]^2$ $k[B][C]$ $k[B][C]^2$ NONE OF THESE
- An endothermic reaction has a forward activation energy of 120 kJ/mol . The activation energy for the reverse reaction will be a) greater or b) less than 120 kJ/mol ?

6. The rate of a reaction has SI units of $\text{mol}/\text{m}^3 \text{ s}$. The empirical rate law is overall second order. What are the SI units on the reaction constant?
7. At 25°C , a reaction with an activation energy of 120.5 kJ/mol has a rate of 0.742 mol/L s . What is the reaction rate at 30°C ?
8. What assumption must apply in order to use change in concentration with time as a measure of a reaction rate?
9. What two assumptions must apply in order to use change in pressure with time as a measure of reaction rate?
10. The graph below on the right shows concentrations of A, B, and C as a function of time. Measured values are shown as circles or squares. The lines are theoretical curves.

a) At initial time ($t = 0$), which species has the greatest rate of formation?

b) Determine the average rate of reaction of A measured over the interval from 1 h to 2 h. Circle the points that you use to calculate the value.

c) Is the instantaneous theoretical rate of reaction of A at $t = 1 \text{ h}$ faster or slower than the measured average over the interval from 1 h to 2 h?



11. The data below are for the reaction $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$. The reaction is known to be first order in A and second order overall.

$[\text{A}]_o$ (mol/L)	$[\text{B}]_o$ (mol/L)	rate (mol/L s)
1.00	0.030	2.5×10^{-3}
1.00	0.040	_____

a) Complete the table with the missing value of reaction rate.

b) Determine the rate constant from the data given in the above table.

12. For a certain reaction that includes species X, a graph of $\ln[X]$ versus time in seconds produces a straight line with a constant slope of $+2.0 \times 10^{-3} \text{ s}^{-1}$.
- Is $[X]$ being produced or consumed during the reaction?
 - What is the reaction order in $[X]$?
13. An empirical reaction rate expression is always a true expression of the reaction mechanism (True or False)?
14. A reaction is inverse first order in $[X]$. When $[X]$ is doubled, by what factor does the reaction rate change?
15. The reaction $P + Q \rightarrow R$ is zero order in $[P]$ and second order in $[Q]$. A container starts with $[P]_o = 1.000 \text{ M}$, $[Q]_o = 0.100 \text{ M}$, and $[R]_o = 0$. After exactly one minute, the concentration of Q has decreased by 10%. What is the rate constant of the reaction?
16. The first order half-life of a certain species is 53.5 yr. How long is required for the concentration of the species to decrease to 25% of its initial value?
17. The rate of a reaction doubles when temperature increases from 25°C to 35°C . What is the activation energy of the reaction (kJ/mol)?
18. According to collision theory, what three conditions must be satisfied for two molecules to react?
19. For a certain reaction at STP, the reactants start at 20 kJ/mol, the activation energy of the forward reaction is 50 kJ/mol, and the activation energy of the reverse reaction is 200 kJ/mol.
- Draw an diagram showing the reaction energy as a function of reaction progress.
 - Determine the enthalpy of the forward reaction.
20. The two reactions below are elemental steps in an overall reaction.
- $$A + B \rightarrow C + D \quad \text{fast} \qquad C + E \rightarrow B + D \quad \text{slow}$$
- What is the expected empirical expression for the rate of formation of D (r_D)?
 - The measured value of r_D is 2.5 mol/L min . What is the rate of reaction of A?
21. A rate expression derived from a reaction mechanism can always be expressed as a simple empirical rate expression (True or False)?

22. What is the reaction order of all elementary reaction steps in a reaction mechanism?
23. What two factors can a catalyst change to increase the rate of a chemical reaction?

Equilibrium

1. State whether each statement below will always be a true way to tell that a chemical reaction has definitely reached equilibrium. Put yes (Y) or no (N).

- a) The rate constants of the forward and reverse reactions are equal. _____
- b) No chemical reactions are occurring. _____
- c) The concentrations of reactants and products are constant. _____

2. Consider the reaction $\text{CO(g)} + 1/2 \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)}$.

- a) What is the expression for the reaction quotient Q ?
- b) When total pressure is increased, will reactants or products be favored?
- c) What is the value of Δn in the expression $K_p = K_c(RT)^{\Delta n}$?
- d) An isotopic labelling experiment is run for the reaction starting only with C^{18}O and O_2 . If equilibrium was NOT dynamic, which species would NOT be found? Circle all that apply.



3. A gas phase reaction system $\text{A(g)} + 2\text{B(g)} \rightleftharpoons \text{C(g)} + \text{D(g)}$ is allowed to reach equilibrium.

- a) The final pressures of components are measured to be $p_A = 0.10$ bar, $p_B = 0.050$ bar, $p_C = 0.70$ bar, and $p_D = 0.15$ bar. What is the value of $K_{eq,P}$?
- b) Less product is created as temperature increases. Is the reaction endo- or exo-thermic?
- c) At 25°C , the value of $K_{eq,C}$ is 2.5×10^{13} . What is the value of $K_{eq,P}$?

4. A reaction $2\text{A(l)} + 3\text{B(aq)} \rightleftharpoons \text{C(s)} + 2\text{D(aq)}$ is run at 25°C where $K_{eq,C} = 3.5 \times 10^{-5}$. The equilibrium concentration of B is 0.5000 M. What is the equilibrium concentration of D?

5. A liquid phase reaction $\text{A(aq)} + \text{B(aq)} \rightleftharpoons 2\text{C(aq)}$ starts with $[\text{A}] = [\text{A}]_o$, $[\text{B}] = [\text{B}]_o$ and $[\text{C}] = [\text{C}]_o$. The equilibrium constant is $K_{eq,C}$. Set up an ICE table and derive the exact equation that should be used to solve this problem for the equilibrium value of [C]. Your equation should be in the form $K_{eq,C} = f(\epsilon)$, where ϵ is the unknown extent of reaction.

6. Consider the two reactions listed below with their respective equilibrium constants.



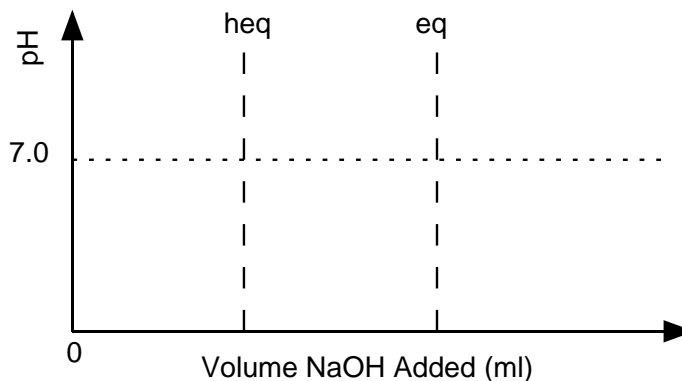
What is the equilibrium constant for the reaction $\text{A} + 3\text{B} \rightleftharpoons 2\text{D} + 2\text{E}$?

13. Explain why $[\text{V}(\text{H}_2\text{O})]^{3+}$ is a stronger acid than $[\text{V}(\text{H}_2\text{O})]^{2+}$.
14. Write the Brønsted reaction that occurs when KCl and NH_4^+ are reacted in water.
- Identify the acids and bases on both sides of the reaction.
 - Determine whether reactants or products are preferred.
 - Determine whether the solution is acidic, basic, or neutral. If this is indeterminate, explain why.
15. Consider equal molar solutions of $\text{Cl}(\text{CH}_2\text{COOH})(\text{aq})$ and $\text{I}(\text{CH}_2\text{COOH})(\text{aq})$. Which solution has the greater pH?

Acid/Base Aqueous Equilibrium

1. What are the two requirements of a useful buffer solution?
2. What is the pH of an aqueous ammonium chloride + ammonia buffer solution at its half-equivalence point?
3. A crime lab technician must titrate 25.0 ml of 0.0500 M HCN with 0.0750 M NaOH.

a) On the axes on the right, sketch the approximate shape of the titration curve. Be sure your pH values are appropriately placed at the markings for the initial (V added = 0), half-equivalence (heq), and equivalence (eq) points.

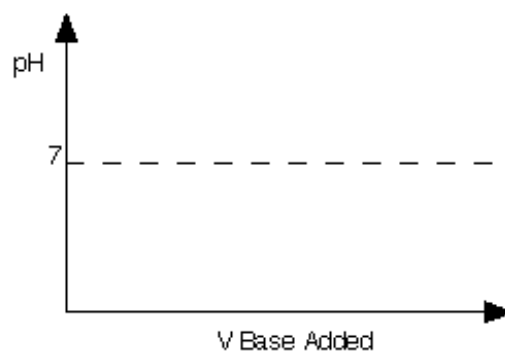


- b) What volume of titrant is needed to reach the equivalence point (eq)?
4. An acid with $K_a = 2.0 \times 10^{-7}$ at 0.250 M is titrated with a base at 0.150 M.
 - a) What is the pH of the solution at the half-equivalence point?
 - b) What is the pH of the solution at the equivalence point?
 5. The K_{sp} value of NaNO_3 is 3.7×10^{-11} . What concentration of NaNO_3 dissolves in water?
 6. Water saturated with $\text{Pb(OH)}_2(\text{aq})$ has $\text{pH} = 9.15$. What is the K_{sp} of $\text{Pb(OH)}_2(\text{aq})$?
 7. Consider the three pairs of solutions given below. Answer YES or NO as to whether the pair forms a good buffer solution when mixed.

	GOOD BUFFER?
a) $\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{NaCH}_3\text{CO}_2(\text{aq})$	_____
b) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq})$	_____
c) $\text{H}_2\text{SO}_4(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq})$	_____
 8. The concentration of Mg^{2+} in an aqueous solution is 1.5×10^{-6} M. Solid NaOH is added. What concentration of NaOH in the final solution will cause Mg(OH)_2 to precipitate? $K_{sp}(\text{Mg(OH)}_2) = 5.6 \times 10^{-12}$.

9. The formation constant of $\text{Ag}(\text{CN})_2^-$ (aq) is 5.6×10^{18} and K_{sp} for AgI is 8.5×10^{-17} . What is $K_{eq,C}$ for dissolving solid AgI in a solution containing CN^- (aq) to form $\text{Ag}(\text{CN})_2^-$ (aq)?
10. A solution of NH_3 has a concentration of 0.150 M. What concentration of NH_4Cl solution is needed to make a buffer with a pH of 8.8? $pK_b(\text{NH}_3) = 4.74$, $pK_a(\text{NH}_4^+) = 9.25$
11. A 100.00 ml solution of base at 0.130 M concentration is titrated with an acid at 0.075 M concentration. What volume of acid is needed to reach the equivalence point?
12. A saturated solution of BaF_2 has $[\text{Ba}^{2+}] = 3.6 \times 10^{-3}$ M. What is the solubility product of BaF_2 ?

13. a) Using the axes on the right, draw the approximate shape of a titration curve for a weak acid ($K_a = 4.0 \times 10^{-7}$) being titrated with a strong base. Mark and label the curve at the half-equivalence and equivalence points.



- b) What is the pH of the solution at the half-equivalence point.

Entropy and Gibbs Free Energy

- Which has the higher entropy, a) CO at STP or b) CO₂ at STP?
- Which has the higher entropy, a) CO₂ at 1 atm, 100 °C or b) CO₂ at STP?
- Consider the following reaction and data:

$$2\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CH}_3\text{OH}(\text{g})$$

	\bar{S}° (J/K mol)	$\Delta_f \bar{G}^\circ$ (kJ/mol)
CH ₄ (g)	186.26	-50.8
O ₂ (g)	205.07	0
CH ₃ OH(g)	126.8	-161.96

- Calculate the standard entropy of reaction.
 - Calculate the standard free energy of reaction.
 - Calculate the standard enthalpy of reaction.
- State any one (and only one) of the four laws of thermodynamics (0th, 1st, 2nd, or 3rd). Define which law you are stating.
 - For the next three problems, consider the reaction given below.

$$\text{PbCl}_2(\text{s}) \rightarrow \text{Pb}(\text{s}) + \text{Cl}_2(\text{g}) \quad \Delta_{rxn} S^\circ = 151.9 \text{ J/K} \quad \Delta_{rxn} H^\circ = 359.41 \text{ kJ}$$
 - Calculate the entropy change of the universe for the reaction running at STP.
 - Calculate the free energy of reaction at 400 °C. Assume entropy and enthalpy are temperature independent.
 - At STP, does the above reaction favor reactants or products?
 - A freshly cut apple left on a table exposed to air will turn brown. From this observation, what can definitely be said to be true about the oxidation process? Choose only ONE answer!
 - The oxidation reaction is exothermic.
 - The oxidized apple is in a higher state of disorder than the fresh apple.
 - Oxygen from the air becomes more disordered during the reaction.
 - All of the above statements must be true.
 - The observation does not pre-determine any of the above conclusions.
 - What is the zeroth law of thermodynamics?

8. A reaction has a standard free energy of 16.37 kJ/mol. Calculate the equilibrium constant for the reaction.

9. The statement that, entropy of the universe always increases (for a spontaneous process) was first stated in what language?

10. Consider the reaction $A + 2B \rightarrow C$ with data below.

	A	B	C
\bar{S}° (J/K mol)	10.0	2.8	7.4
$\Delta\bar{H}^\circ$ (kJ/mol)	-13.0	-14.0	-11.0

a) Determine standard entropy change of reaction.

b) Determine the standard Gibb's free energy change of reaction.

11. To obtain useful work from a chemical reaction, what must be true under all conditions?

a) The reaction must be exothermic.

b) The products must have a higher entropy than the reactants.

c) Both of the above statements must always be true.

d) None of the above must necessarily be true.

Electrochemistry

1. Write the balanced redox reaction for the electrochemical cell notation shown below. (2)



2. Is a yttrium/zirconium fuel cell used as an oxygen sensor in a car a) an electrolytic or b) a voltaic cell?
3. Write a balanced half-cell electrochemical reaction for $\text{Fe} \rightarrow \text{Fe}(\text{OH})_2$ in acidic solutions.

For the next two questions, consider two half-cell reduction reactions



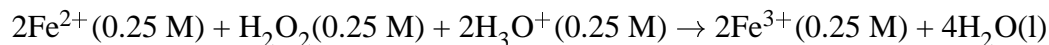
where $E_{\text{cell},\text{A}}^{\circ} < E_{\text{cell},\text{B}}^{\circ}$.

4. Which reaction will occur at the cathode of an electrolytic cell?
5. Which reactant, A^+ or B^+ , is the stronger oxidizing agent?
6. Consider the two reduction half-cell reactions shown below.



The reactions are set up in an electrochemical cell with the reaction of A at the anode and the reaction of B at the cathode. The standard cell potential is measured as -1.110 V. What is the standard half-cell reduction potential of the reaction of B?

7. Consider the reaction shown below carried out in aqueous solution.

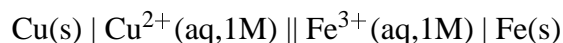


- a) The standard cell potential is 1.15 V. Calculate the measured cell potential.
- b) The standard cell potential is 1.15 V. What is the equilibrium constant of the reaction?
8. The reaction $\text{AuCl}_4^-(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s}) + 4\text{Cl}^-(\text{aq})$ produces 2.5 mg of Au and a current of 3.5 A in an electroplating cell. How long did the reaction run? $M_{\text{Au}} = 196.9665 \text{ g/mol}$
9. An electrochemical cell can contain a salt bridge or a _____ to allow flow of ions between the two chambers.
10. Write the balanced net ionic reaction for MnO_4^- reacting with Fe^{2+} to produce Mn^{2+} and Fe^{3+} in acidic solutions.

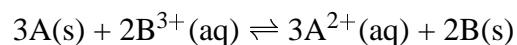
11. The net ionic reaction $\text{Zn} + 4\text{H}^+ + 2\text{VO}_2^+ \rightarrow \text{Zn}^{2+} + 2\text{VO}^{2+} + 2\text{H}_2\text{O}$ is balanced for acidic solutions. What is the balanced reaction for basic solutions?

12. A voltaic cell will produce a positive value of $V_{\text{cathode}} - V_{\text{anode}}$. True or False?

13. Write the balanced overall redox reaction for the following electrochemical cell:



14. A cell has a standard cell potential of 1.35 V. The redox reaction is




a) When the cell concentrations are $[\text{A}^{2+}] = 2.50 \text{ M}$ and $[\text{B}^{3+}] = 0.0150 \text{ M}$, what is the cell voltage at 25°C ?

b) What is the equilibrium constant for the redox reaction?

15. A cell for the electrolysis of NaCl(l) to Na(l) uses 25 kA (kilo-Amps) of current. What mass of Na(l) is produced per second? $M_{\text{Na}} = 22.9898 \text{ g/mol}$

Transition Metals

- Which reaction produces red-brown rust?
 - $\text{Fe(s)} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2$
 - $\text{Fe(s)} + \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$
 - $\text{Fe(s)} + \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
- Which of the above reactions is anaerobic?
- Explain why the density of transition metals varies based on atomic radii and atomic mass.
- Pyrometallurgy is used when a transition metal is typically found in what type of compound as an ore?
- Consider the coordination compound $[\text{Ni}(\text{NO}_2)_2(\text{en})_2]\text{Cl}$.
 - What is the oxidation state of Ni?
 - What is the coordination number of Ni?
- Name the compound $\text{Na}[\text{Pd}(\text{NH}_3)(\text{NO}_2)_3]$, where palladium is in a 2+ oxidation state.
- Consider the complex $[\text{Mn}(\text{L})_6]^{x+}$ where the ligand L is monodentate. Illustrate the d orbital energy level diagram according to crystal field theory. Label the levels correctly ($d_{x^2-y^2}$, d_{z^2} , ...). Use the space to the right.
- Consider the d orbital energy level diagram for a tetrahedral d orbital splitting shown to the right. Label the energy levels and fill in the electrons as spin up or down for a low spin state of Fe^{3+} . Fe: $[\text{Ar}] 3d^6 4s^2$

- Show the electrons for the same Fe^{3+} in a complex with tetrahedral binding, high spin state.
 