ROSES ARE RED AND VIOLETS ARE BLUE

The pigment in hydrangea blossoms belongs to the class of molecules called anthocyanins, or, more particularly, it is a cyanidin. Cyanidins are responsible for the red color of roses, straw berries, rasp-berries, apple skins, rhubarb, and cherries and for the purple color of blueberries. What is more, the color of cyanidins depends on the pH. Red cabbage juice is only red in acid; it is purple in a more neutral solution.

The reason for this shift in color with pH is that the pigment is an acid and can donate an H⁺ ion. As the pH increases, the conjugate base is formed, and this is accompanied by a significant color change. This means that the color is a reflection of the pH of the solution. If the pH could be controlled, then the color could be controlled.

- 1. The ideal range of pH for blue flowers is a pH of 5.5. This means that $[H_3O^+] =$
- 2. The ideal range of acidity to produce pink flowers is $[H_3O^+] = 4.0 \times 10^{-7} M$. This means the pH must be about
- 3. If you wanted to buffer a solution near a pH of 5.5, which system below would you choose?
 - a) A mixture of HCl and NaCl
 - b) A mixture of acetic acid and sodium acetate
 - c) A mixture of ammonia and ammonium chloride
- 4. The cyanidins pictured above are soluble in water. Based on the structure of the molecule, explain briefly but completely, why this should be so.

5. The blue form of cyanidin is illustrated below. Answer the questions regarding formal charge, atom hybridization, and geometry. *Note that lone pairs on the O atoms are not shown*.

C atom hybridization =

6. The blue form is stabilized by adding aluminum salts to the soil. If you add AlCl₃ to water, and its dissolves to produce Al³⁺ (aq) and Cl⁻(aq) ions, is the solution acidic, basic, or neutral?

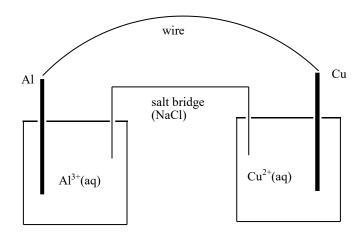
REDOX CHEMISTRY AND MOLECULAR STRUCTURE

Reaction of nicotinamide, a very important biochemical.

- a) Is the reaction below oxidation or reduction?
- c) Fill in the blanks on the figure.
- b) Describe what happens to the geometry and hybridization of the indicated C atom.

ELECTROCHEMISTRY

1. Consider the electrochemical cell below.



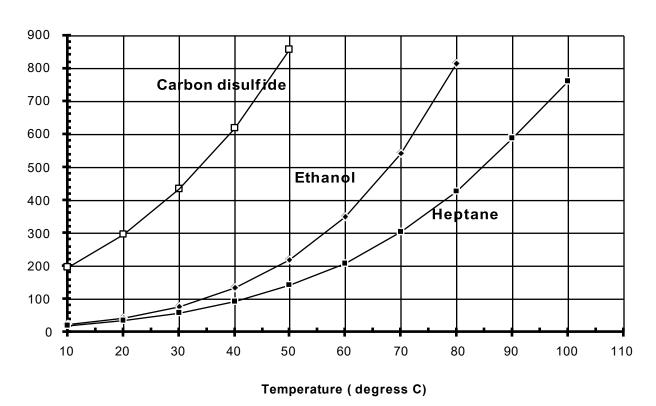
- a) Circle is the better reducing agent, Al or Cu?
- b) Write the balanced reaction for this electrochemical cell?
- c) Which is the anode in the cell, Al or Cu?_____
- d) What is the standard cell potential? E° =_____
- e) Electrons flow in the external wire
- f) Na⁺ ions in the salt bridge flow _____

2. Consider the following reduction half-reaction s:

Half-Reaction	$\mathbf{E}^{\circ}(\mathbf{V})$
$Ce^{4+}(aq) + e^{-} \rightarrow Ce^{3+}(aq)$	+1.61
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2 e^- \rightarrow 2 Hg(l)$	+0.79
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2 e^{-} \to \operatorname{Sn}(s)$	-0.14
$Ni^2+(aq) + 2 e^- \rightarrow Ni(s)$	-0.25
$Al^{3+}(aq) + 3 e^{-} \rightarrow Al(s)$	-1.66

- (a) Which is the weakest oxidizing agent in the list?
- (b) Which is the strongest oxidizing agent?
- (c) Which is the strongest reducing agent?
- (d) Which is the weakest reducing agent?
- (e) Will Sn(s) reduce Ag⁺(aq) to Ag(s)?
- (f) Will Hg(l) reduce Sn²⁺(aq) to Sn(s)?
- (g) Name the ions that can be reduced by Sn(s).
- (h) What metals can be oxidized by Sn^{2+} (aq)?

Intermolecular Forces



Use the vapor pressure curves above to answer the following questions:

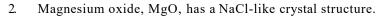
- 1. What is the vapor pressure of heptane at 70 °C?
- 2. What is the normal boiling point of ethanol? _____
- 3. What type of intermolecular force exists
 - a) Between two CS₂ molecules?
 - b) Between two heptane molecules?_____
 - c) between two ethanol molecules?
- 4. Suppose the pressure is 600 mm H g and the temperature is 50 °C. Decide if each substance is a liquid or vapor under those conditions.
 - a) Carbon disulfide _____
 - b) Ethanol _____
 - c) Heptane ____
- 5. Which one or ones of these molecules is expected to dissolve in water?
- 6. Explain briefly why the normal boiling point of ethanol is higher than that of CS₂.
- 7. Why is the normal boiling point of heptane higher than that of CS₂?

SOLIDS

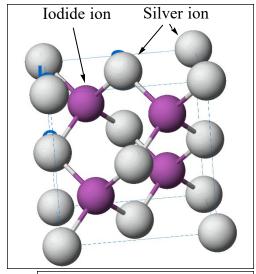
- 1. Silver iodide crystallizes in the unit cell shown here.
- (a) How many silver ions are there in each unit cell?
- (b) How many iodide ions are there in each unit cell?
- (c) What is the solubility of silver iodide in water?

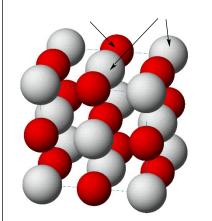
$$AgI(s) \ \leftrightarrow Ag^+(aq) \ + \ I^-(aq)$$

- i) 1.5 x 10⁻¹⁶ mol/L
- ii) 1.2 x 10⁻⁸ mol/L
- iii) $2.4 \times 10^{-8} \text{ mol/L}$
- iv) 0.0012 mol/L

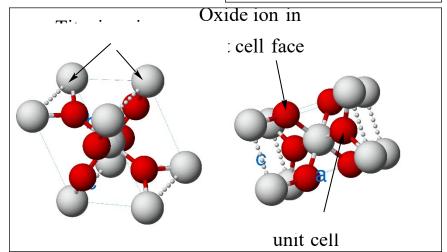


- (a) In which type of unit cell are the M g²⁺ ions arranged (sc, bcc, fcc)? _____
- (b) How many magnesium ions are there per unit cell?





- 3. Two views of the structure of rutile are shown here.
- (a) How many titanium ions are inside the unit cell?
- (b) How many oxide ions are inside the unit cell?
- (c) What is the formula of



(d) What is the charge on the titanium ion in rutile?

KINETICS AND MECHANISMS

1. Iodide ion is oxidized in acid solution by hydrogen peroxide.

$$H_2O_2(aq) + 2 H^+(aq) + 2 I^-(aq) \rightarrow I_2(aq) + 2 H_2O(l)$$

A proposed mechanism is

Step 1 slow
$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + OI^-(aq)$$

Step 2 fast
$$H^+(aq) + OI^-(aq) \rightarrow HOI(aq)$$

Step 3 fast
$$HOI(aq) + H^{+}(aq) + I^{-}(aq) \rightarrow I_{2}(aq) + H_{2}O(l)$$

- (a) What is the molecularity of the first step?
- (b) Write the rate law for the rate determining step.
- (c) Identify any intermediates in the elementary steps in this reaction.
- 2. Radioactive radon-222 (222Rn) from natural sources can seep into the basement of a home. The half-life for the first order 222Rn is 3.8 days.

What is the rate constant for the decay of ²²²Rn?

- a) 0.182 day^{-1}
- b) 0.263 day⁻¹
- c) 3.80 day⁻¹
- d) 5.50 day⁻¹

If your basement has $4x10^{13}$ atoms of 222 Rn per liter, and the radon gas is trapped in your basement, how many atoms of 222 Rn will remain after 7.6 days?_______ How much will remain after one month (31.0 days)?

- a) 1.2×10^{10} atoms
- b) 1.4×10^{11} atoms
- c) 1.3×10^{12} atoms
- d) 1.0×10^{13} atoms
- e) None of the above!

CHEMICAL EQUILIBRIA

1. The equilibrium involving CO, Cl₂, and phosgene has been thoroughly studied. (Although quite poisonous, phosgene is a very important industrial intermediate in chemical manufacture.)

$$CO(g) + Cl_2(g)$$
 , $COCl_2(g)$

(a) Write the equilibrium constant expression for this reaction.

$$K_c = \dots$$

	[CO]	[Cl ₂]	[COCl ₂]
Initial concentration (M)	0.0102	0.00609	0
Change in concentration (M)			
Equilibrium concentration (M)		0.00301	

- (b) A mixture of CO and Cl₂ is placed in a flask. The initial concentrations are given in the table. After equilibrium has been achieved at 600 K, [Cl₂] now has a value of 0.00301 M. *Complete the table above by entering a numerical value in each cell.*
- (c) Using the data in your table, calculate the value of K c.

2 An important reaction in the environment and in industry is the *endothermic* decomposition of calcium carbon ate.

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$$

Predict the effect of the following changes on the position of equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made:

- a) Adding more CaCO₃
- b) Lowering the temperature
- c) Adding more CO₂
- d) Increasing the size of the container for the reaction.

ACIDS, BASES, & SOLUBILITY

1. Use the acid-base chart to decide on the relative strengths of the following acids: (a) acetic acid, CH $_3$ CO $_2$ H (b) HNO $_3$ (c) ammonium ion (d) H $_2$ S

weakest strongest

- 2. Conjugate acids and bases.
 - a) Consider the reaction of hydrazine with the hydrogen sulfate ion.

 $N_2H_4(aq) + HSO_4^-(aq) \leftrightarrow N_2H_5^+(aq) + SO_4^{2-}(aq)$

On the left side of the equation, the Brønsted acid is _____ and the Brønsted base is _____

b) Complete and balance the following acid-base reaction:

 $_$ N H₄⁺(aq) + $_$ CO ₃²-(aq) \rightarrow $_$

Does the equilibrium in this reaction lie to the right or to the left? _______

- 3. Predict the relative pH for each of the following salts. That is, state whether each solution has a pH greater than 7 (>7); less than 7 (<7); or equal to 7 (=7).
 - (a) Na₂SO₄
 - (b) LiNO₃
 - (c) CuCl₂
 - (d) K_2CO_3
 - (e) NaB(OH)₄
- 4. Calculate the pH of a 0.10 M solution of ammonium chloride? Show work
 - (a) 1.80
 - (b) 2.37
 - (c) 3.74
 - (d) 5.12
 - (e) 11.63

5. Acid-Base Reactions

- a) After you mix 5 mL of 0.20 M CH $_3$ CO $_2$ H with 5 mL of 0.20 KOH, does the resulting solution have a pH =7, pH < 7, or pH > 7? _______
- b) Does the pH increase, decrease, or stay the same when you add water to a solution of 0.2 M CH₃CO₂H and 0.1 M NaCH₃CO₂?
- 6 What is the pH of a buffer solution made by adding 24.0 g of NaH₂PO₄ (molar mass = 120 g/mol) and 14.2 g of Na₂HPO₄ (molar mass = 142 g/mol) to 500 mL of water?
 - (a) 4.1
 - (b) 6.9
 - (c) 7.2
 - (d) 7.5
 - 7. Calcium carbonate, $CaCO_3$, is considered very poorly soluble in water. Its solubility can be *estimated* using its K_{sp} value. The calculation assumes that the ions produced, Ca^{2+} and CO_3^{2-} do not react further in solution. What would happen to the solubility of $CaCO_3$ if some of the carbonate ion reacted with water? Would the solubility increase, decrease, or stay the same? *Explain briefly!*

$$CO_3^{2-}(aq) + H_2O(aq) \rightarrow HCO_3^{-}(aq) + OH^{-}(aq)$$

8 Name or give correct formulas for two insoluble salts of the hydroxide ion.

a) _____

b)

9. In each case below, decide if a precipitate will form when mixing the indicated reagents (answer yes or no):

 $\underline{\hspace{1cm}} NaF(aq) + Ba(NO_3)_2(aq)$

 $\underline{\qquad} KCl(aq) + Mg(NO_3)_2(aq)$

 $\underline{\hspace{1cm}}$ Na₂SO₄(aq) + AgNO ₃(aq)