12. What is the mass percent of ammonium dichromate in water solution if 25 g ammonium dichromate $\left((NH_4)_2Cr_2O_7\text{, molar mass: } 252.1\text{ g}\right)$ is dissolved in 100. g water?

(A) 1.8%
(B) 20%
(C) 25%
(D) 80%
(E) 100%

13. A standard solution of sodium hydroxide can be used in a titration experiment to determine the molar mass of a solid acid. A common mistake in such a titration experiment is the failure to rinse the buret with the standard solution after the final water rinse but before measurements of the volume of the standard solution are taken. This mistake accounts for which of the following results?

I. The reported volume of the standard solution used in the titration reaction is too small.

II. The reported volume of the solute used to dissolve the unknown acid is too small.

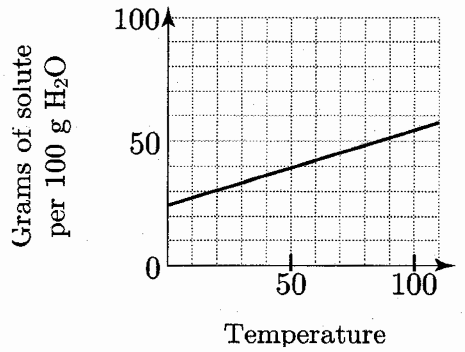
III. The reported number of moles of unknown acid used in the titration reaction is too large.

(A) I only
(B) II, and III only
(C) III only
(D) I and III only
(E) I, II, and III

14. The level of arsenic permitted in drinking water is 0.050 ppm (parts per million). Which of the following is another way to express that same concentration?

(A) 0.050 mg As/milliliter H_2O
(B) 0.050 mg As/liter H_2O
(C) 0.050 g As/million liters H_2O
(D) 0.050 mg As/million liters H_2O
(E) 0.050 mg As/million grams H_2O

Questions 15 and 16: refer to the solubility curve for KCl in water as shown below.



15. At what temperature is the concentration of a saturated solution of KCl (molar mass: 74.5 g) approximately 3 molal?
    - (A) 0°C
    - (B) 35°C
    - (C) 50°C
    - (D) 80°C
    - (E) 100°C

16. What is the mass percentage of water in a saturated solution of KCl at 80°C?
    - (A) 20%
    - (B) 33%
    - (C) 50%
    - (D) 67%
    - (E) 80%

Questions 17 and 18: refer to the solubility curve for KCl in water as shown above. A mixture containing 100 g H_2O and 40. g KCl is warmed to 60°C and stirred thoroughly. It is then cooled to 40°C with no immediate change in appearance.

17. The resulting solution is best described as
    - (A) colloidal
    - (B) isotonic
    - (C) unsaturated
    - (D) saturated
    - (E) supersaturated

18. When a tiny crystal of KCl is added to the cooled solution, a quantity of white crystalline solid forms. Which is the best description of the mass of the solid phase that forms in the system at 40° C?
    - (A) 0 g solid
    - (B) 2 g solid
    - (C) 10 g solid
    - (D) 20 g solid
    - (E) 55 g solid

19. Which accounts for the Tyndall effect in colloids?

(A) scattering of light by particles of matter
(B) absorption of light by particles of matter
(C) absorption of light of specific wavelength in the visible range
(D) absorption of light of specific wavelength in the ultraviolet range
(E) alternating patterns of refraction and reflection of light by lattice particles

20. A hydrophobic colloid is most likely to be stabilized in water by the presence of

(A) sodium ions, Na^+
(B) benzene molecules, C_6H_6
(C) hydrogen ions, H_3O^+
(D) sucrose molecules, $C_{12}H_{22}O_{11}$
(E) stearate ions, $C_{17}H_{35}COO^-$

21. Which applies to a 1.0 molar solution of potassium nitrate in water?

I. Adding water raises the freezing point.
II. Adding water increases the vapor pressure of the solution.
III. Adding water decreases the density of the solution.

(A) I only
(B) II and III only
(C) I and III only
(D) II and III only
(E) I, II, and III

22. Compared to water, a 0.20 *M* solution of NaCl will have all of the following properties EXCEPT

(A) greater density
(B) lower vapor pressure
(C) lower boiling point
(D) lower freezing point
(E) greater conductivity

23. In a spontaneous, exothermic dissolving process, which of these values has a negative sign?

    I. ΔG_{soln}
    II. ΔH_{soln}
    III. ΔT

    (A) I only
    (B) III only
    (C) I and II only
    (D) II and III only
    (E) I, II, and III

24. A saturated solution of KNO_3 in equilibrium with excess solute is prepared at 20°C. Which of the following describes the solution after the temperature of the system is increased to 40°C while still in contact with excess solute?

    I. The molality of the solution increases.
    II. The solution remains saturated.
    III. The density of the solution increases.

    (A) II only
    (B) III only
    (C) I and III only
    (D) II and III only
    (E) I, II, and III

25. A dilute solution of NaCl is prepared at 20°C. Which of the following describes the solution after the temperature of the solution is increased to 40°C?

    I. The vapor pressure of the solution increases.
    II. The number of ion pairs in solution increases.
    III. The difference between the freezing point and the boiling point of the solution increases.

    (A) I only
    (B) III only
    (C) I and II only
    (D) I and III only
    (E) I, II, and II

Free-Response Questions

26. Answer the following questions concerning propanone (acetone, C_3H_6O), a substance used to remove nail polish.
    - (A) Draw a Lewis structure for propanone.
    - (B) Is propanone expected to be soluble in water? Explain.
    - (C) A solution is prepared by combining 30.0 mL propanone (density: 0.792 g mL^{-1}) with 50.0 mL 2-propanol (C_3H_7OH, density 0.785 g mL^{-1}). Assume that the volumes are additive.
        - (1) Calculate the percent by mass of 2-propanol in the solution.
        - (2) Calculate the percent by volume of propanone in the solution.
        - (3) Calculate the mole fraction of propanone in the solution.
    - (D) Compare the expected freezing point of solution described in part (B) to the freezing point of pure 2-propanol. Is the freezing point of the solution expected to be higher than, equal to, or lower than the freezing point of the pure solvent? Explain.

27. Answer each of the following questions related to the dissolving process.
    - (A) Identify the two major energy changes that determine whether the dissolving of any solid in water is exothermic or endothermic. Define each energy change.
    - (B) When an ionic solid dissolves in water, the sign for ΔS is positive. Explain.
    - (C) Discuss the effect of each energy change defined in part (A) on the solubility of an ionic solid.
    - (D) Discuss the role of free energy change, ΔG, in determining the solubility of a solute/solvent pair.
    - (E) The dissolving process for ammonium nitrate, NH_4NO_3, in water is endothermic.
        - (1) When 0.10 mol of NH_4NO_3 is added to 100 mL of water at 298 K, will the temperature of the resulting solution be higher than, lower than or the same as the initial temperature of the water? Explain.
        - (2) How will this observation of temperature be different if the amount of NH_4NO_3 is doubled? Explain.

28. Answer the following questions related to the procedures for preparing solutions in the laboratory. Distilled water and ordinary laboratory equipment are available for use.

(A) Describe the measurements and procedures needed to prepare a 1.0 *M* (1.0 molar) solution of H_2SO_4 (molar mass 98 g) in water using 49 g of H_2SO_4. Concentrated sulfuric acid is nearly 100% H_2SO_4. It is available as a dense liquid with known specific gravity.

(B) Different procedures are used when the solution of H_2SO_4 is to be prepared at 1.0 *m* (1.0 molal) concentration? Explain.

(C) Which of the two solutions – 1.0 molar or 1.0 molal – has the greater percent by mass H_2SO_4? Explain.

(D) Compared to the dissolving of alcohol in water, what additional precautions should be taken when preparing a solution of sulfuric acid in water? Explain.

(E) The two major changes associated with the dissolving of any solid in water are crystal lattice energy and hydration energy. Which is larger for an endothermic dissolving process? Explain.

CHAPTER 5

STOICHIOMETRY

STOICHIOMETRY: CHEMICAL CALCULATIONS

Stoichiometry is the branch of chemistry that deals with quantitative measurements associated with chemical reactions. In practical terms for the AP chemistry student, the term refers to many of the quantitative problems encountered as listed below. You need to be able to use the mole concept for measuring quantities of chemical elements and compounds in chemical reactions.

<u>Chemical formulas</u>: formula mass and percentage composition; empirical and molecular formulas; hydrated salts

<u>Chemical elements and compounds</u>: Moles, molar mass, molar volume, the Avogadro number

<u>Chemical reactions</u>: mass, volume and moles of reactants and products; yield: theoretical, actual and percent yield; limiting reactant

Many students just call these "mole problems". **Dozens are for counting doughnuts, reams are for counting paper, moles are for counting atoms (and molecules).**

One way to look at quantitative problem solving is to identify the information provided, then identify the information to be determined. Effective management of stoichiometry problems is NOT based on memorizing a series of steps for each problem type. It is based on establishing a mental mindset for yourself that produces a reliable problem-solving strategy.

One mole of any substance is one gram-formula-weight of that substance

18 grams of water, H_2O
98 grams of sulfuric acid, H_2SO_4
342 grams of sucrose, $C_{12}H_{22}O_{11}$

Any one molecule of sulfuric acid, H_2SO_4, weighs about 5 times as much as a molecule of water, H_2O.

One mole is also the Avogadro number of particles of the substance identified.

6.02×10^{23} molecules of water, H_2O
6.02×10^{23} molecules of sulfuric acid, H_2SO_4
6.02×10^{23} molecules of sucrose, $C_{12}H_{22}O_{11}$

We use this information in factors that look like this

$$\frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O} \qquad \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342 \text{ g } C_{12}H_{22}O_{11}}$$

$$\frac{6.02 \times 10^{23} \text{ molecules } H_2SO_4}{1 \text{ mol } H_2SO_4}$$

$$\frac{6.02 \times 10^{23} \text{ atoms S}}{1 \text{ mol S}}$$

$$\frac{6.02 \times 10^{23} \text{ ions Na}^+}{1 \text{ mol Na}^+ \text{ ions}}$$

We use moles to help us count atoms by weighing. We can count by weighing because all molecules of a given substance have the same mass (weight).

Chemical Formulas

When dealing with chemical formula-oriented problems, a situation maybe presented where a chemical formula is known and some other information is to be determined. A chemical formula tells the relationship between numbers and types of atoms in a substance, perhaps as simple He (helium gas) or more complex such as $(NH_4)_4Fe(CN)_6 \cdot 3H_2O$, (ammonium ferrocyanide trihydrate).

When the formula is given, the problem assigned is likely to be to count the atoms of each component, then determine the mass percent of one or more components.

You probably established the mindset for this kind of problem a long time ago:

- get the mass of each part
- add up all the parts to get a total mass
- then get a percent for each.

In the opposite case, information on mass or percent by mass is given. You are assigned to calculate the ratio of atoms – that is the empirical formula (*empirical* means based on observation or experiment; in the context of chemistry problem-solving, an empirical formula is the simplest whole number ratio of atoms in the formula for a chemical compound). Alternatively, you may be asked to use a set of information to determine a chemical formula. Be sure to make full use of any information given. For example, if the information supplied says a hydrated binary salt of osmium is 54.2% by mass osmium and 15.4% water, what is the formula of the hydrated salt? Additional information that can be inferred is that the percent by mass of chlorine is 30.4. From there it is small step in logic to determine how to solve this problem.

You need to determine the ratio of atoms. First, you can look up how much one mole of atoms weighs. Then you can easily find out how many atoms of each element is contained in a known sample.

mass of atoms → number of moles of atoms → ratio of number of moles of atoms

In the case of this problem, the most convenient sample is 100. grams, from which you can immediately claim the composition as 54.2 g Os, 30.4 g Cl, and 15.4 g H_2O. Now, you can look up the atomic mass of each element (and the molar mass of H_2O - in case you forgot that it's 18 g/mol). Next, determine the number of moles of atoms of each; then you get a fractional ratio of moles of atoms of each which you can simplify to smallest whole number since you already passed 7$^{\text{th}}$ grade math.

$$54.2 \text{ g Os} \times \frac{1 \text{ mol Os}}{190 \text{ g Os}} = 0.285 \text{ mol Os}$$

$$30.4 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.5 \text{ g Cl}} = 0.856 \text{ mol Cl}$$

$$15.4 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18 \text{ g } H_2O} = 0.856 \text{ mol } H_2O$$

Ratio: $Os_{0.285} \quad Cl_{0.856} \quad (H_2O)_{0.856}$

$$Os_{\frac{0.285}{0.285}} \quad Cl_{\frac{0.856}{0.285}} \quad (H_2O)_{\frac{0.856}{0.285}}$$

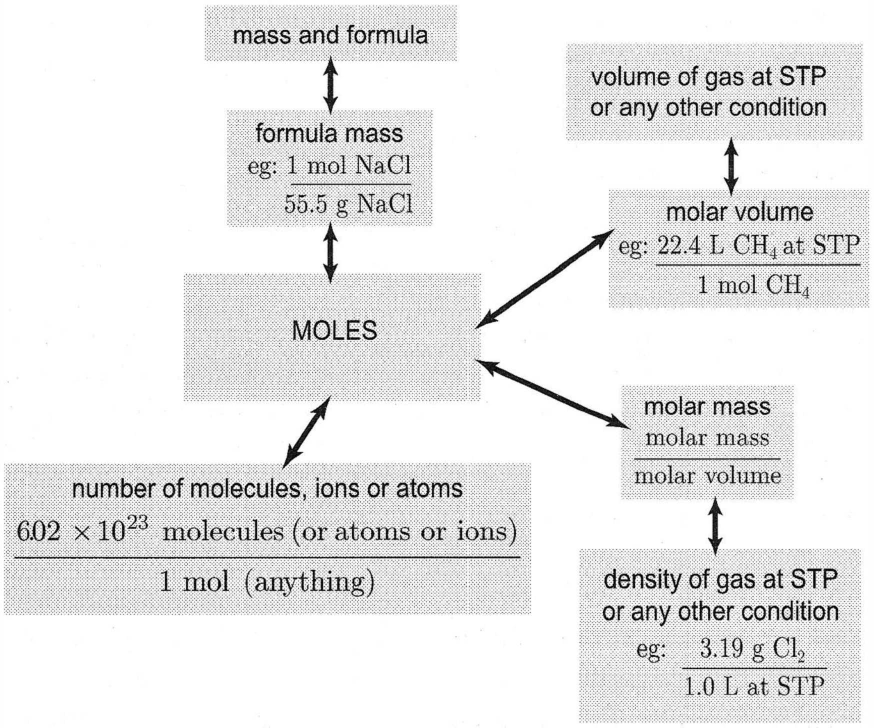
$$OsCl_3 \cdot 3H_2O$$

When more about moles is needed

Pushing a little further ahead, the information provided could be formula, mass, moles, volume of a gas at specified conditions, actual numbers of molecules, ions or atoms or even mass per unit volume (density). The assigned problem could be to determine one or more of the components of information not given.

The starting point for any of this is the molar mass using atomic masses from the Periodic Table. Start from anywhere, get moles, then go anywhere else. Figure 5.1 will help organize your strategies for solving "mole problems".

Figure 5.1



NOW FOR SOME ACTUAL CHEMICAL REACTIONS

Substances react one atom or even one mole of atoms at a time. In order to deal with quantities of reactants and products, we need a way to count the atoms. Because all atoms or molecules of a given substance have the same mass, it is convenient to count atoms or molecules by weighing.

Quantitative problems dealing with chemical reactions typically present a reaction with its corresponding chemical equation and one or more quantities of reactants. You could also be assigned to provide a desired quantity of product. Your task is to determine an unknown quantity such as quantity of product expected to be produced, and asked to determine the quantity of reactant to be supplied. In its simplest form, a question might ask you to determine what mass of silver phosphate is produced when 2.35 g $AgNO_{3(s)}$ is added to excess $H_3PO_{4(aq)}$. ("Excess" means that there is more than enough H_3PO_4 to react with all the $AgNO_3$. It also means that you don't need to think about a "limiting reactant" - see below.)

You need to write the balanced chemical equation for this reaction (looks like double replacement)

$$3AgNO_3 + H_3PO_4 \rightarrow Ag_3PO_4 + 3HNO_3$$

and remind yourself that the equation says

> three moles $AgNO_3$ of reacts with one mole of H_3PO_4 to form one mole of Ag_3PO_4 and three moles of HNO_3

Once you get moles of $AgNO_3$, you can get moles, then mass, of anything else in this reaction.

$$2.35\text{ g AgNO}_3 \times \frac{1\text{ mol AgNO}_3}{170\text{ g AgNO}_3} \times \frac{1\text{ mol Ag}_3\text{PO}_4}{3\text{ mol AgNO}_3} \times \frac{419\text{ g Ag}_3\text{PO}_4}{1\text{ mol Ag}_3\text{PO}_4} = 1.93\text{ g Ag}_3\text{PO}_4$$

The limiting reactant

A further complication emerges when two quantities of reactants are given, then the limiting reactant must be determined and that value used to determine other quantities in the reaction.

In terms of the problem above, let's say that the conditions became an experiment in which 2.35 g $AgNO_3(s)$ is added to 1.58 g H_3PO_4 in water solution.

> This is the same problem as above except that there are now two possibilities: either you use all the $AgNO_3$ or you use all the H_3PO_4.
>
> You need to determine moles of each reactant, then determine the moles of one consumed if all the other is consumed, knowing that 3 mol $AgNO_3$ is needed for each mol of H_3PO_4. One of these is the limiting reactant – the reactant that is totally consumed.
>
> Once you get moles of moles of limiting reactant, you can get moles of anything else in this reaction including moles of the excess reactant consumed and moles left unreacted. Once you have moles of these substances, you can determine any mass that is needed.

... and how much product you actually get – YIELD

There are two kinds of yield – how much that you predict can be produced based on moles of reactants and how much is actually produced that you can collect and weigh (count the atoms and molecules) after the reaction is completed. The predicted quantity is the amount determined as above, where we assumed full conversion to product. In actual practice, side reactions and other confounding events occur to decrease the amount of product. The amount actually produced is the actual yield. Percent yield is the fractional expression of mass actually produced as a fraction of the amount that could have been produced. We express that fraction as grams (or moles) actually produced per 100 grams (or moles) theoretically produced – parts per hundred or per cent.

> Mindset: same as above for theoretical moles of product. Then weigh (count the atoms and molecules) the product that is actually produced. Convert this to a fraction with 100 grams of theoretical yield as the denominator.

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

III. Reactions

B. Stoichiometry

1. Ionic and molecular species present in chemical systems; net ionic equations
2. Balancing of equations including those for redox reactions
3. Mass and volume relations with emphasis on the mole concept, including empirical formulas and limiting reactants

from the list of CHEMICAL CALCULATIONS

1. Percentage composition
2. Empirical and molecular formulas from experimental data
3. Molar masses from gas density, freezing-point, and boiling point measurements
5. Stoichiometric relations using the concept of the mole; titration calculations

Stoichiometry – a range of quantitative problems through stoichiometry of mixtures and limiting/excess reactants

from the list of EQUATIONS & CONSTANTS

Believe it or not, this table actually identifies n as [number of] moles, m as mass and M as molar mass (whenever it doesn't mean molarity).
Avogadro's number = 6.022×10^{23} [molecules] mol^{-1} is also provided.

The relation $n = m/M$ is also given. If you need that as a reference, you are in the wrong exam.

from the list of RECOMMENDED EXPERIMENTS

9. Determination of mass and mole relationship in a chemical reaction
16. Analytical gravimetric determination

Nearly every laboratory activity calls for use of stoichiometry – counting the atoms and molecules – that are being used or produced. Whenever the directions include use of weighed quantities, these are actually quantities with a known number of moles of molecules, ions or atoms.

Multiple Choice Questions

1. Which of these alkaline earth metal oxides has the greatest percent by mass of oxygen?

   (A) barium oxide
   (B) beryllium oxide
   (C) calcium oxide
   (D) magnesium oxide
   (E) strontium oxide

2. Which expression gives percent by mass of carbon in oxalic acid, $H_2C_2O_4 \cdot 2H_2O$?

   (A) $\frac{2}{14} \times 100$
   (B) $\frac{12}{90} \times 100$
   (C) $\frac{24}{66} \times 100$
   (D) $\frac{24}{90} \times 100$
   (E) $\frac{24}{126} \times 100$

3. Which oxides of manganese, Mn, have percent by mass of manganese that is greater than 50%?

   I. MnO
   II. MnO_2
   III. Mn_2O_3

   (A) II only
   (B) III only
   (C) I and III only
   (D) II and III only
   (E) I, II, and III

4. Which describes the resulting system when 0.40 moles of $Na_2CO_{3(s)}$ is added to 0.50 liters of 0.60 molar $CuCl_2$ solution?

   (A) A blue precipitate forms; excess $CO_3{}^{2-}$ is found in solution.
   (B) A blue precipitate forms; excess Cu^{2+} is found in solution.
   (C) A blue precipitate forms; no excess reactants are found in solution.
   (D) A nearly colorless homogeneous system forms; excess $CO_3{}^{2-}$ is found in solution.
   (E) A nearly colorless homogeneous system forms; excess Cu^{2+} is found in solution.

5. Which pair of samples contains the same number of oxygen atoms in each compound?

(A) 0.10 mol Al_2O_3 and 0.50 mol BaO

(B) 0.20 mol Cl_2O and 0.10 mol HClO

(C) 0.20 mol SnO and 0.20 mol SnO_2

(D) 0.10 mol Na_2O and 0.10 mol Na_2SO_4

(E) 0.20 mol $Ca(OH)_2$ and 0.10 mol $H_2C_2O_4$

6. Consider the reaction

$$2Na_3PO_{4(aq)} + 3ZnCl_{2(aq)} \rightarrow Zn_3(PO_4)_{2(s)} + 6\ NaCl_{(aq)}$$

A precipitate is formed when 0.20 moles of sodium phosphate, Na_3PO_4, is mixed with 0.80 moles of zinc chloride, $ZnCl_2$, in water solution. Which lists the ions in water solution after the reaction occurs, in order of increasing concentration?

(A) Na^+, Cl^-, Zn^{2+}, $PO_4{}^{3-}$

(B) Zn^{2+}, $PO_4{}^{3-}$, Na^+, Cl^-

(C) $PO_4{}^{3-}$, Zn^{2+}, Na^+, Cl^-

(D) $PO_4{}^{3-}$, Zn^{2+}, Cl^-, Na^+

(E) Zn^{2+}, $PO_4{}^{3-}$, Cl^-, Na^+

7. Consider the reaction

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$

Which value is closest to the mass of $ZnO_{(s)}$ produced when 50.0 g $ZnS_{(s)}$ is heated in an open vessel until no further weight loss is observed?

(molar masses: O_2 – 32 g, SO_2 – 64 g, ZnO – 81 g, ZnS – 97 g)

(A) 25 grams

(B) 40 grams

(C) 50 grams

(D) 60 grams

(E) 75 grams

8. Consider the reaction

$$2Al_{(s)} + 3Cl_{2(g)} \rightarrow 2AlCl_{3(s)}$$

Which expression gives the volume of Cl_2 consumed, measured at 1 atm and 273 K, when 25.0 g Al reacts completely with Cl_2 according to the above equation?

(A) $25.0 \times \frac{3}{2} \times \frac{22.4}{2}$

(B) $\frac{25.0}{22.4} \times \frac{3}{2} \times \frac{22.4}{2}$

(C) $25.0 \times \frac{27}{1} \times \frac{3}{2} \times \frac{22.4}{1}$

(D) $25.0 \times \frac{1}{27} \times \frac{3}{2} \times \frac{22.4}{1}$

(E) $25.0 \times \frac{1}{27} \times \frac{2}{3} \times \frac{22.4}{1}$

9. Which sample contains the greatest number of nitrogen atoms? (All measurements taken at 1 atm and 273 K.)

(A) 0.20 mol $N_2O_{4(g)}$

(B) 0.40 mol $N_{2(g)}$

(C) 40. L $NO_{2(g)}$

(D) 40. g $NH_{3(g)}$

(E) 80. g $N_2O_{4(g)}$

10. $$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{\cancel{(g)}}$$

Propane gas, $C_3H_{8(g)}$, burns according to the equation above. A mixture containing 0.030 moles of $C_3H_{8(g)}$ and 0.200 moles of $O_{2(g)}$ is placed in a rigid container and its pressure measured. The mixture is ignited. Which describes the contents of the container after maximum reaction has occurred and the system returned to its original temperature?

(A) 0.050 mol $O_{2(g)}$ remains unreacted and the pressure has increased.

(B) 0.050 mol $O_{2(g)}$ remains unreacted and the pressure has decreased.

(C) 0.170 mol $O_{2(g)}$ remains unreacted and the pressure has decreased.

(D) 0.020 mol $C_3H_{8(g)}$ remains unreacted and the pressure has decreased.

(E) 0.020 mol $C_3H_{8(g)}$ remains unreacted and the pressure has increased.

11. When the equation for the reaction below is balanced using smallest whole numbers, which gives a correct description of the information in the equation?

$$..?..\ Sc(NO_3)_3 + ..?..\ NaOH \rightarrow ..?..\ Sc(OH)_3 + ..?..\ NaNO_3$$

I. The number of ions represented is 20.
II. The number of atoms represented is 22.
III. The sum of the coefficients is 8.

(A) II only
(B) III only
(C) I and II only
(D) II and III only
(E) I, II, and III

12. An unidentified compound is reported to contain 77.5% manganese and 22.5% oxygen by mass. Which set of values when substituted for x and y gives the best representation of the empirical formula for the unidentified compound?

$$Mn_xO_y$$

(A) $\frac{77.5}{54.9}$ and $\frac{16.0}{22.5}$

(B) $\frac{77.5}{54.9}$ and $\frac{22.5}{16.0}$

(C) $\frac{54.9}{22.5}$ and $\frac{16.0}{77.5}$

(D) $\frac{54.9}{77.5}$ and $\frac{16.0}{22.5}$

(E) $\frac{54.9}{22.5}$ and $\frac{16.0}{77.5}$

13. What minimum volume of 0.200 M Na_2CO_3 is needed to precipitate all the Sr^{2+} from 25.0 mL of 0.100 M $Sr(NO_3)_2$?

(A) 6.25 mL
(B) 12.5 mL
(C) 25 mL
(D) 50 mL
(E) 100 mL

14. $$Cu_{(s)} + 4HNO_{3(aq,conc)} \rightarrow 2NO_{2(g)} + Cu(NO_3)_{2(aq)} + 2H_2O$$

What volume of $NO_{2(g)}$ measured at 1 atm and 273 K can be produced by the reaction of 0.750 mol copper with excess concentrated nitric acid according to the equation above?

(A) 11.2 liters
(B) 22.4 liters
(C) 33.6 liters
(D) 44.8 liters
(E) 67.2 liters

15. $$Al^{3+} + 3e^{-} \rightarrow Al^{0}$$

In the half-reaction shown above, the term $3e^{-}$ represents

(A) $3 \times 96{,}500$ electrons

(B) $3 \times 6.02 \times 10^{23}$ electrons

(C) $3 \times 6.02 \times 10^{23}$ coulombs

(D) $\frac{3}{27} \times 96{,}500$ electrons

(E) $\frac{3}{27} \times 6.02 \times 10^{23}$ electrons

16. Consider the combustion of ethane as shown in the equation below.

$$2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(g)}$$

What quantity of reactant remains after ignition of a mixture that contains 0.60 moles of C_2H_6 mixed with 2.50 moles of O_2? (Assume maximum reaction according to the equation above.)

(A) 0.20 mol O_2
(B) 0.40 mol O_2
(C) 1.90 mol O_2
(D) 0.20 mol C_2H_6
(E) 0.30 mol C_2H_6

Questions 17-19: A mixture is prepared by adding 100. mL of 0.10 M Na_2CrO_4 to 100. mL of 0.10 M $AgNO_3$. A precipitate forms in this mixture. The precipitate is separated from the mixture by filtration.

17. What is the concentration of Na^+ in the reaction mixture after filtration?

(A) 0.050 M
(B) 0.10 M
(C) 0.15 M
(D) 0.20 M
(E) 0.40 M

18. What quantity of solid product is produced?

(A) 0.0025 mol
(B) 0.0050 mol
(C) 0.010 mol
(D) 0.015 mol
(E) 0.020 mol

19. Which describes the changes in concentration of the spectator ions, Na^+ and NO_3^- in the reaction mixture as the reaction occurs in the beaker containing $AgNO_{3(aq)}$?

	$[Na^+]$	$[NO_3^-]$
(A)	increases	remains the same
(B)	remains the same	decreases
(C)	remains the same	remains the same
(D)	increases	decreases
(E)	decreases	decreases

20.
$$2Al_{(s)} + 3S_{(s)} \rightarrow Al_2S_{3(s)}$$

What mass of Al_2S_3 is produced when 1.50 moles of aluminum reacts with excess sulfur according to the equation above?

(A) 40.5 g
(B) 48.0 g
(C) 61.5 g
(D) 75.0 g
(E) 113 g

21. When 0.60 mol ZnS was roasted in pure oxygen, 0.40 mol SO_2 was collected. Which best describes the contents of the solid phase remaining in the crucible?

(A) no excess ZnS; 0.60 mol ZnO
(B) no excess ZnS; 0.30 mol ZnO
(C) 0.20 mol excess ZnS; 0.30 mol ZnO
(D) 0.20 mol excess ZnS; 0.40 mol ZnO
(E) 0.30 mol excess ZnS; 0.40 mol ZnO

22. The mass of element X found in 1.0 mole each of four different compounds is 28 g, 42 g, 56 g and 84 g, respectively. Which of the following is a possible atomic mass for element X?

(A) 14
(B) 28
(C) 35
(D) 42
(E) 49

23. Which value is closest to the volume of $O_{2(g)}$ measured at STP that could be produced when 0.20 mol $KClO_{3(s)}$ is heated according to the equation below?

$$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$$

(A) 4.5 L
(B) 6.7 L
(C) 7.5 L
(D) 15. L
(E) 34. L

24. How many moles of $KCl_{(s)}$ should be added to 0.500 liters of 0.20 M $CrCl_3$ solution to increase the chloride concentration to 1.00 M? (Assume no change in volume.)

(A) 0.20
(B) 0.40
(C) 0.50
(D) 0.60
(E) 0.80

25. Epsom salt, $MgSO_4 \cdot 7H_2O$, (molar mass: 246 g) can be dehydrated by heating in an open crucible. Which value is closest to the fraction of the mass of salt in the crucible lost when the crucible is heated to constant weight?

(A) $\frac{1}{8}$
(B) $\frac{1}{7}$
(C) $\frac{1}{4}$
(D) $\frac{1}{3}$
(E) $\frac{1}{2}$

Free-Response Questions

26. An unknown hydrocarbon, C_xH_y, exists as two isomers at 298 K; one is a gas, the other is a liquid.

    (A) When 3.90 grams of this hydrocarbon is placed in a 3.00 liter container and heated to 800. K, no liquid remains and the pressure becomes 1.58 atm. What is the molar mass of this hydrocarbon?

    (B) When the hydrocarbon is burned in oxygen, the only products formed are water and carbon dioxide. The mixture of products is 76.5% by mass $CO_{2(g)}$.What is the empirical formula of this hydrocarbon?

    (C) What is the molecular formula of this hydrocarbon? What is the IUPAC name of this hydrocarbon? Write the balanced equation for the complete combustion of this hydrocarbon.

27. A common rocket propellant is a mixture that includes liquid hydrazine, N_2H_4, as a fuel and liquid hydrogen peroxide, H_2O_2, as oxidizer. The products formed are nitrogen, $N_{2(g)}$, and water $H_2O_{(g)}$.

    (A) Write a balanced chemical equation for the reaction of N_2H_4 with H_2O_2.

    (B) What volume of $N_{2(g)}$ measured at 0.975 atm and 298 K is produced when 100. grams of $H_2O_{2(l)}$ is consumed?

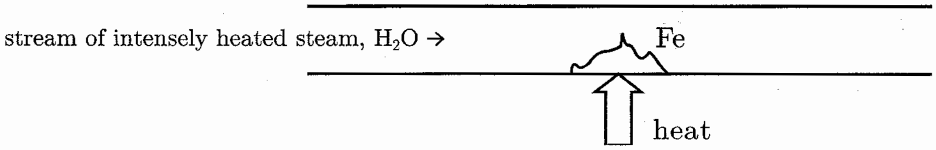
    (C) Some standard enthalpies of formation ΔH_f°, at 298 K are given below:

$H_2O_{(g)}$	-241.6 kJ mol^{-1}
$N_2H_{4(l)}$	50.2 kJ mol^{-1}
$H_2O_{2(l)}$	-192.3 kJ mol^{-1}

    Using these values, calculate the standard enthalpy of reaction, ΔH°, for the reaction written in part (A).

    (D) If all of the energy produced by the reaction in part (B) is transferred to 5.00 kg of water at 20.0°C, what is the final temperature of the water? (The specific heat capacity of water is 4.18 J g^{-1} °C^{-1}.)

28. When iron is treated with excess steam and heated intensely, it is converted to Fe_3O_4, the laboratory version of the mineral, magnetite. Hydrogen gas is the other product of this reaction.



(A) Write the balanced equation for this reaction.

(B) Calculate the oxidation number of iron in Fe_3O_4.

(C) A sample of 25.0 g iron is heated intensely under a stream of hot steam. After this treatment, the increase in mass of the solid residue is 3.75 g.

(1) Determine the percent by mass of Fe_3O_4 in the solid residue.

(2) Calculate the number of moles of iron that remains unchanged.

(D) In the reaction described in part (C), what volume of hydrogen gas, measured at STP, was produced?

CHAPTER 6

CHEMICAL KINETICS

The study of reaction rates and mechanisms, also known as kinetics, is a key topic of the AP Chemistry program. Kinetics from the perspective of the differential rate law has had substantial exposure in many AP Exams over the years. Coverage of integrated rate law and the Arrhenius equation was recently restored to the AP Chemistry curriculum. You should be prepared to address reaction kinetics on both sections of the exam.

MOLECULES (AND IONS) IN COLLISION

You should be able to visualize the fundamental ideas of reaction kinetics via the **collision model**, an extension of the Kinetic Molecular Theory (KMT) that helps explain chemical change. The collision model describes chemical reactions as the summary effect of many, many collisions between potential reactant particles. Most collisions are ineffective and do not lead to a chemical reaction. Those that are effective "react" - that is, atoms get rearranged to produce a different substance.

Collisions

In order to be part of an **effective collision**, the reacting particles must be traveling fast enough – with enough kinetic energy – so that their collision transfers sufficient energy to break existing bonds. Furthermore, to be effective, this collision must occur with sufficiently favorable orientation so that new chemical bonds can form. Thus an effective collision must satisfy both a **kinetic energy** requirement and an **orientation** (or **steric**) requirement. You should be able to explain why an increase in temperature leads to more collisions, as well as more effective collisions. You should be able to explain why increases in concentration and surface area allow for more collisions. **Catalysts** change the rate of a reaction by diminishing the activation energy of a reaction. You should be able to make a sketch that shows why a surface catalyst diminishes the activation energy by trapping one reactant in a favorable orientation. A summary of the factors that affect rate of reaction is found in Figure 6.1. You should be able to explain why the presence of a catalyst accounts for more effective collisions. The **Arrhenius equation** incorporates both of these ideas.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad R = 8.134\ \text{J mol}^{-1}\ \text{K}^{-1}$$

It is usually presented in a line-slope format that compares frequency of effective collisions at two different temperatures. Calculating the slope of the line thus drawn allows you to determine the **activation energy** of the reaction.

<u>More and more effective collisions</u>. **Reaction rate** is usually measured in mols, mL or mmHg per unit time. Reaction rate increases when temperature or concentration increases or when a catalyst is present. Using principles from the KMT and the collision theory, you should be able to explain why such changes occur. Figure 6.2 provides a good summary.

Figure 6.1 Factors affecting the rate of a reaction

- Temperature - at higher temperature, molecules collide with greater transfer of energy
- Concentration, including pressure for gas phase systems - at higher concentrations, the number of collisions increases
- Phase/surface/homogeneity of the system - provides for more favorable collision geometry
- Presence of a catalyst - catalyst provides a more favorable activated complex with lower requirement for energy of activation.

Reaction mechanism and reaction order

A **reaction mechanism** is a step-by-step description of the series of events, usually collisions, that lead to a reaction. The slowest step in that series determines the overall rate of the reaction and is known as the **rate determining step**. The **molecularity** of the reaction describes the number of reacting particles in the collision and can be uni-, bi- or (rarely) ter-molecular.

The **reaction order** describes the effect on the overall rate of a change in the concentration of a specific reactant. **First order,** where the rate change is directly proportional to the change in reactant concentration, is most common. **Second order** reactants change rate proportional to the square of the change in reactant concentration. Changes in concentration for **Zero** order reactants have no effect on the overall rate of the reaction. A **rate law** shows the overall rate of reaction as a function of the **rate constant** and the concentration of each reactant raised to the appropriate order. Figure 6.2 provides a good comparison of reaction orders.

Figure 6.2 Chemical Kinetics: comparing reaction order

	ORDER		
	Zero	**First**	**Second**
Rate law	Rate $= k[\mathrm{A}]^0$	Rate $= k[\mathrm{A}]^1$	Rate $= k[\mathrm{A}]^2$
Integrated rate law	$[\mathrm{A}] = -kt + [\mathrm{A}]_0$	$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0$	$\frac{1}{[\mathrm{A}]} = kt + \frac{1}{[\mathrm{A}]_0}$
Plot needed to give a straight line	$[\mathrm{A}]$ versus t	$\ln[\mathrm{A}]$ versus t	$\frac{1}{[\mathrm{A}]}$ versus t
Relationship of rate constant to the slope of straight line	Slope $= -k$	Slope $= -k$	Slope $= k$
Half-life	$t_{\frac{1}{2}} = \frac{[\mathrm{A}]_0}{2k}$	$t_{\frac{1}{2}} = \frac{0.693}{k}$	$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$

The Maxwell-Boltzmann energy distribution graph in Figure 6.3 shows the distribution of kinetic energies for the same sample of gas molecules at different temperatures. Note that the curve at higher temperature has a greater fraction of molecules that possess the minimum energy required to start the reaction, E_a.

The graph of concentration of reactants as in Figure 6.4 (starting high and diminishing over time) and the products (starting low and increasing over time) shows that a chemical equilibrium is reached when both curves reach a horizontal line.

Figure 6.3 Energy distribution

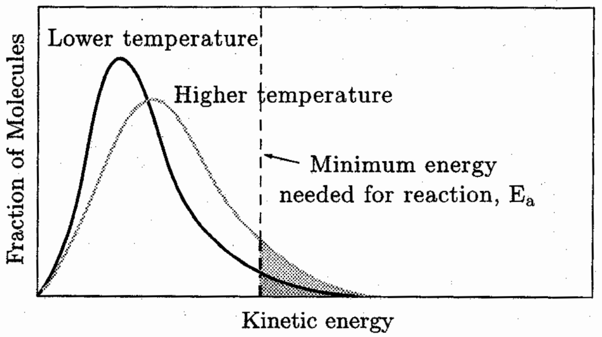
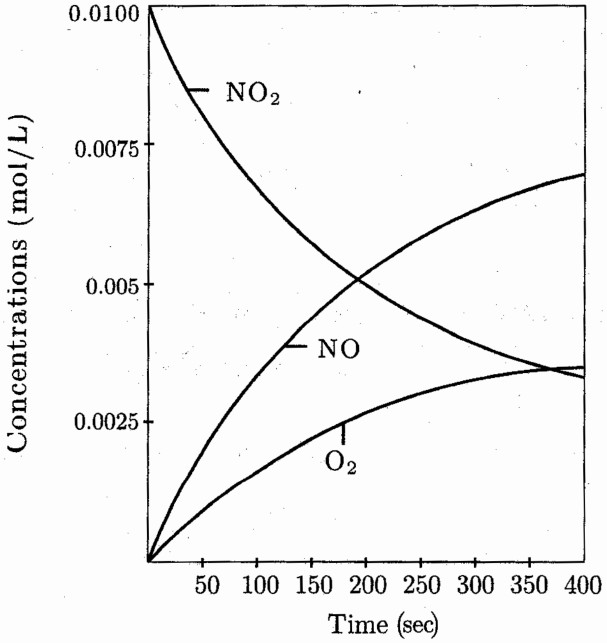


Figure 6.4 $NO + \frac{1}{2}O_2 \rightarrow NO_2$ **Tracking changes in concentration**



VOCABULARY: REACTION KINETICS

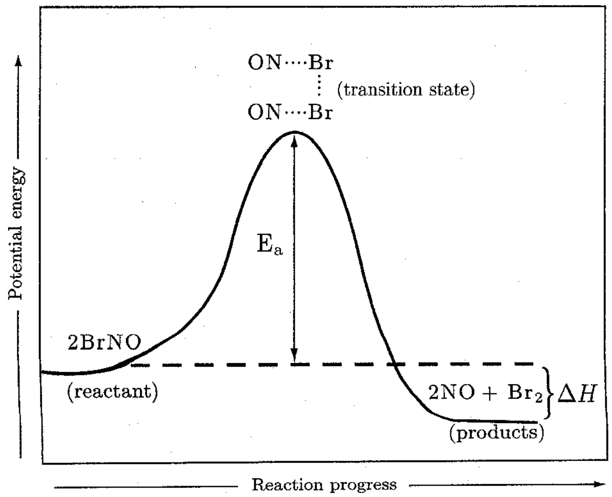
Reaction rates

Kinetics	the study of reaction rates and mechanisms
Reaction Rate	number of molecular events occurring per unit of time ($\Delta C/\Delta t$) For the given reaction: $aA + bB \rightarrow dD + eE$ Overall Reaction rate: $\frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} = \frac{1}{e}\frac{\Delta[E]}{\Delta t}$ Relative rate of consumption: $\frac{-\Delta[A]}{\Delta t}$
Half-life	time required for the concentration of a reactant to decrease by one-half of its original value
Catalyst	substance that increases the rate of a reaction by providing a mechanism with lower activation energy for the reaction

Reaction mechanisms

Reaction mechanism	the stepwise description of the processes by which reactant species change into products
Elementary Reaction	(or process)– one step within a reaction mechanism • **Unimolecular**– one molecule breaks into two pieces or undergoes a rearrangement to form a new isomer • **Bimolecular** – two molecules collide and combine or transfer atoms • **Termolecular** – three molecules collide and combine or transfer atoms
Rate-determining step	the one elementary step in the reaction mechanism that is significantly slower than others. This step limits or determines the overall rate of the reaction.
Activation Energy (E_a)	energy barrier that must be overcome in order for reactants to convert to products; potential energy acquired during the formation of the activated complex from the kinetic energy of the colliding reactants, as shown in Figure 6.5

Figure 6.5 Reaction coordinate (Potential energy diagram)



Rate law and reaction order

Rate Law	mathematical expression that links the rate of a reaction to the concentrations of the substances that influence the rate of that reaction Rate = $k[\mathrm{A}]^{y}[\mathrm{B}]^{z}$, where k is the rate constant and y and z are exponents that specify the order for reactants A and B, respectively
Rate Constant	k, the proportionality constant in the rate law for a given reaction; k changes with temperature
Reaction order	the exponent on a given concentration term within the rate law; a reactant is: • 1st order — when the concentration of a reactant is doubled and the reaction rate doubles • 2nd order — when the concentration of the reactant is doubled and the reaction rate increases by a factor of 4 • 0 order — when the concentration of reactant is changed and there is no change in the reaction rate
Overall reaction order	sum of the individual orders in the rate law
Isolation experiment	kinetics experiment which isolates the effect of one particular reactant on the reaction rate; carried out by making the starting concentration of that particular reactant significantly lower than the concentrations of the other reactants

THE MATHEMATICS OF SIMPLE REACTION KINETICS

Differential rate law data:

Compare the change in initial concentration of one reactant and its effect on initial reaction rate while holding the other reactant(s) constant. Example: for the reaction hypothetical A + B → AB, consider this data set.

Trial	**Initial [A]**	**Initial [B]**	**Initial rate**
1	x	y	1.01
2	2x	y	2.02
3	x	2y	2.02

Compare trial 1 to trial 2 and note that, although the initial concentration of B is held constant at y, the concentration of A doubles from x to 2x. This concentration change causes the reaction rate to double, so the order of reactant A is said to be 1 or first order. Comparing trials 1 and 3 reveals that, although reactant A is held constant at x, the concentration of reactant B is doubled from y to 2y. This change in concentration also causes the initial rate of reaction to double, so reactant B is also said to be first order. The overall order of the reaction is the sum of the individual orders, in this case, second order overall.

Use differential rate laws to determine order of reactants, overall order of each reaction and rate constant from experimental data; predict reaction mechanism.

Integrated Rate Law Data:

The set of rate data for this type of experiment is shown in a different way: the concentration of a reactant is presented as a function of time, thus giving an indication of the instantaneous rate of disappearance of the reactant at a given time, *t*. To determine the order of a reactant, plot concentration versus time and look for a straight line relationship for some function of [C] vs. *t*.

Use integrated rate law data to establish the graphical relationship between concentration of reactant (some function of [C]) and reaction time, *t*, to determine order of each reactant, overall order of reaction and rate constant from experimental data; predict reaction mechanism.

Order	**Straight line relationship**
0 order:	[C] vs. time
1st order:	ln[C] vs. time
2nd order:	1/[C] vs. time

Since many reactions are first order, try graphing ln[C] versus *t* first; then try 1/[C] versus *t* to investigate 2nd order; then try [C] versus *t* as a test of zero order.

When the linear relationship of the natural log of the concentration of reactant C versus time, then this reaction is first order in C. Other straight line relationships are given above.

The Arrhenius equation and its applications

The Arrhenius equation includes the concept of the effective collision, which is based on particles traveling with sufficient kinetic energy to break old bonds and colliding in an orientation which then allows a new bond to form. It is usually presented in a line-slope format that compares frequency of effective collisions at two different temperatures. Calculating the slope of the line thus drawn allows you to determine the **activation energy, E_a**, of the reaction. This relationship is given by the equation

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad R = 8.134 \text{ J mol}^{-1}\text{ K}^{-1}$$

where k_1 refers to the rate constant at temperature T_1 and k_2 at T_2. Note well that E_a is typically given in kJ so R must be adjusted to kJ as well. All temperatures must be noted in kelvins to agree with R. You may wish to refer to this graph in your textbook.

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

III. Reactions

D. Kinetics

1. Concept of rate of reaction
2. Use of experimental data and graphical analysis to determine reactant order, rate constants, and reaction rate laws
3. Effect of temperature change on rates
4. Energy of activation; the role of catalysts
5. The relationship between the rate-determining step and a mechanism

from the list of CHEMICAL CALCULATIONS

11. Kinetics calculations

from the list of EQUATIONS & CONSTANTS

$\ln[A]_t - \ln[\mathrm{A}]_0 = -kt$	associated with first order kinetics
$\dfrac{1}{[\mathrm{A}]_t} - \dfrac{1}{[\mathrm{A}]_0} = kt$	associated with second order kinetics
$\ln k = \dfrac{-E_a}{R}\left(\dfrac{1}{T}\right) + \ln A$	the Arrhenius equation; E_a= activation energy

from the list of RECOMMENDED EXPERIMENTS

12. Determination of the rate of a reaction and its order

Multiple Choice Questions

1. Each of the following is true about a heterogeneous catalyst EXCEPT
   (A) Its presence changes the rate of a chemical reaction.
   (B) It does not undergo a permanent chemical change.
   (C) It is in the same phase as the reacting particles.
   (D) Its presence lowers the activation energy of the overall reaction.
   (E) Its presence decreases the potential energy of the activated complex.

2. Which accounts for the increase in the rate of reaction when a catalyst is added to a reaction system?
   (A) decrease in ΔH for the reaction
   (B) increase in ΔS for the reaction
   (C) increase in potential energy of the reactants
   (D) increase in potential energy of the products
   (E) decrease in potential energy of the activated complex

3. In a system where the reaction $A_{(g)} + B_{(g)} \rightarrow C_{(g)}$ is taking place, which change increases the concentration of $A_{(g)}$?
   I. addition of $A_{(g)}$ molecules at constant temperature and volume
   II. addition of $A_{(g)}$ molecules at constant temperature and pressure
   III. addition of $A_{(g)}$ molecules at constant volume and pressure
   (A) I only
   (B) III only
   (C) II and III only
   (D) I and III only
   (E) I, II, and III

4. All of the following apply to the reaction $A_{(g)} + B_{(g)} \rightarrow C_{(g)}$ as it is carried out at constant temperature in a sealed rigid container EXCEPT
   (A) The total pressure decreases.
   (B) The rate of reaction decreases.
   (C) The entropy of the system decreases.
   (D) The number of molecules of C decreases.
   (E) The frequency of collisions between molecules A and B decreases.

5. Consider the hypothetical reaction

$$X_{(g)} + 2Y_{(g)} \rightarrow XY_{2(g)}$$

$$\frac{\Delta[Y]}{\Delta t} = -5.0 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$$

What is the rate of formation of $XY_{2(g)}$?

(A) -5.0×10^{-2} mol L^{-1} sec^{-1}
(B) -2.5×10^{-2} mol L^{-1} sec^{-1}
(C) 1.0×10^{-2} mol L^{-1} sec^{-1}
(D) 2.5×10^{-2} mol L^{-1} sec^{-1}
(E) 5.0×10^{-2} mol L^{-1} sec^{-1}

Question 6-11: Consider the reaction and its rate law given below:

$$2A_{(g)} + B_{(g)} \rightarrow C_{(g)}$$

$$\text{Rate} = k[A]^2[B]$$

At the beginning of one trial of this reaction [A] = 4.0 and [B] = 1.0. The observed rate was 0.048 mol C L^{-1} sec^{-1}.

6. The numerical value of k, the rate constant, for this reaction is closest to

(A) 3×10^2
(B) 4×10^0
(C) 8×10^{-1}
(D) 1×10^{-2}
(E) 3×10^{-3}

7. Which is the label for k, the rate constant?

(A) mol^2 L^{-2} sec^{-1}
(B) L mol^{-2} sec^{-1}
(C) L^2 mol^{-2} sec^{-1}
(D) L^2 sec mol^{-1}
(E) L^2 sec mol^{-2}

8. When [B] becomes 0.4 mol L^{-1}, what will be the value of [A]?

(A) 0.8 mol L^{-1}
(B) 1.6 mol L^{-1}
(C) 2.8 mol L^{-1}
(D) 3.4 mol L^{-1}
(E) 3.6 mol L^{-1}

9. Which of the following describes how the rate for this trial of the reaction, at constant temperature, changes as [B] approaches 0.4 mol L^{-1}?

(A) The rate decreases because the concentration of the products increases.
(B) The rate remains the same because the rate constant remains the same.
(C) The rate remains the same because the temperature remains the same.
(D) The rate decreases because the concentration of the reactants decreases.
(E) The rate remains the same because the energy of activation remains the same.

10. Which applies to this reaction as it proceeds at constant temperature?

I. The rate of the reaction decreases.
II. The effectiveness of collisions between reactant molecules remains the same.
III. The frequency of collisions between reactant molecules remains the same.

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

11. Which applies to this system when its temperature increases at constant volume?

I. [A] decreases at a greater rate.
II. The value for k, the rate constant, remains the same.
III. The rate of the reaction increases.

(A) I only
(B) II only
(C) I and III only
(D) II and III only
(E) I, II, and III

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12. All of the following increase the rate of a reaction involving a solid EXCEPT

(A) adding more of the solid
(B) increasing the concentration of the solid
(C) increasing the temperature
(D) adding a catalyst
(E) increasing the surface area of the solid

Questions 13–17: $5Br^-_{(aq)} + BrO_3{}^-_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(\ell)} + 3H_2O_{(\ell)}$

The reaction between bromide ions and bromate ions in acidic water solution occurs according to the equation above. The rate law for this reaction is known to be

$$\text{Rate} = k[Br^-][BrO_3{}^-][H^+]^2$$

13. One proposed reaction mechanism has three steps up to and including the slow step. The first step in the reaction mechanism is

$$Br^- + H^+ \rightarrow \text{Intermediate}_1$$

Which statement(s) must be true about this first step in the reaction mechanism?

I. Its coefficients of the reactants must correspond to exponents on those terms in the rate law.

II. No further step can include Intermediate$_1$ as a reactant.

III. A subsequent step must include $BrO_3{}^-$ as a reactant.

(A) I only
(B) II only
(C) III only
(D) I and II only
(E) I and III only

14. The overall order for this reaction is

(A) 2
(B) 3
(C) 4
(D) 6
(E) 12

15. What is the effect of increasing $[H^+]$ in this reaction system at constant temperature?

(A) The value of the rate constant increases.
(B) The potential energy of the products decreases.
(C) The potential energy of the activated complex decreases.
(D) The number of collisions between H^+ and Br^- ions increases.
(E) The effectiveness of collisions between H^+ and Br^- ions increases.

16. What is the effect of adding $Br_{2(\ell)}$ to the system? (Assume negligible change in volume.)

I. The mass of the system increases.

II. The rate of reduction of $BrO_3{}^-$ increases.

III. The rate of oxidation of Br^- decreases.

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

17. Which change will cause a decrease in the rate of the reaction?

I. addition of OH^- ions
II. removal of H^+ ions
III. addition of H_2O molecules

(A) II only
(B) III only
(C) I and III only
(D) II and III only
(E) I, II, and III

---

18. Consider the hypothetical reaction below taking place in a piston at constant temperature. The reaction is started by placing $A_{(g)}$ and $B_{(g)}$ in the piston. No chemical equilibrium is established.

$$A_{(g)} + 2B_{(g)} \rightarrow AB_{2(g)}$$

Which change causes an increase in the partial pressure of $B_{(g)}$?

I. addition of $B_{(g)}$ at constant volume
II. decrease in the volume of the reaction vessel
III. addition of $AB_{2(g)}$ at constant volume

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

19. Which applies to any reaction mechanism?

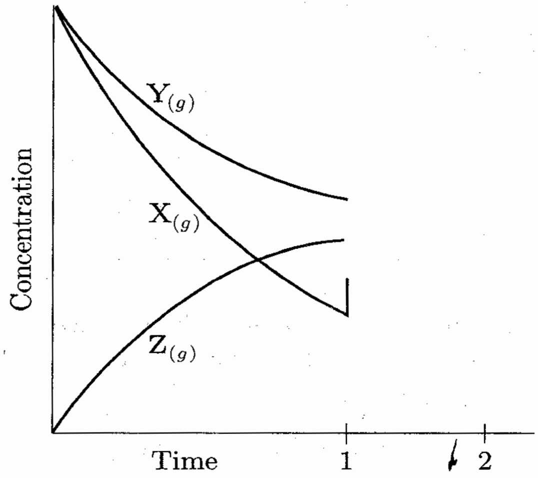
I. It is a list of steps that produce the overall chemical reaction.
II. It includes only unimolecular steps.
III. It cannot include reaction intermediates.

(A) I only
(B) II only
(C) III only
(D) I and II only
(E) I and III only

Questions 20-22: Consider the gas reaction

$$2X_{(g)} + Y_{(g)} \rightarrow Z_{(g)}$$

The graph below represents the changes in concentration of reactants and products between the start of reaction and Time 1.



20. Which event is most likely to have occurred at Time 1?
    (A) addition of X
    (B) addition of Y
    (C) addition of Z
    (D) removal of Y
    (E) removal of Z

21. Which gives the rate of changes in concentrations that occur as the reaction proceeds from Time 1 to Time 2?

	[X]	[Y]	[Z]
(A)	decreases	decreases	decreases
(B)	decreases	increases	increases
(C)	decreases	decreases	increases
(D)	increases	increases	decreases
(E)	increases	increases	increases

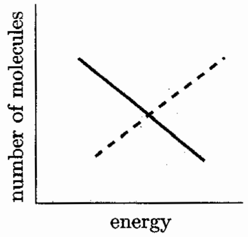
22. When the lines for X, Y and Z are extended to time 2, which feature of those extensions is most closely related to the coefficients of the reactants, X and Y, in the equation for the reaction?
    (A) [Y]
    (B) [Z]
    (C) $\Delta[Z]$
    (D) $\dfrac{\Delta[X]}{\Delta[Y]}$
    (E) $[X] + [Y]$

23. Which energy distribution diagram represents an increase in temperature?

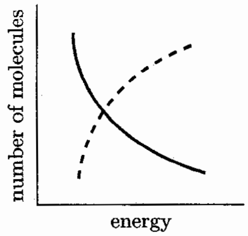
——— before

- - - - after

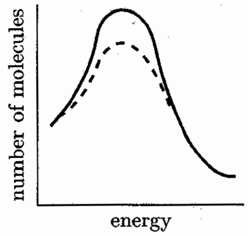
(A)



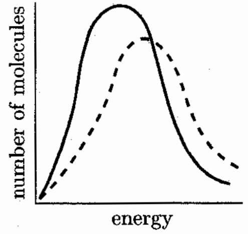
(B)



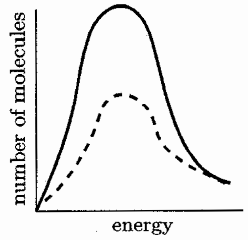
(C)



(D)

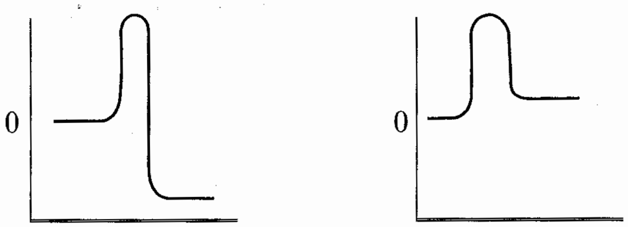


(E)

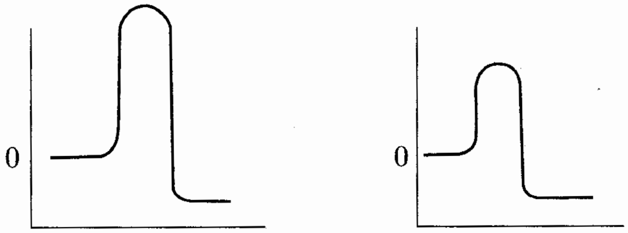


24. Which pair of potential energy/reaction coordinate diagrams represents a comparison between the same reactants where one of the pair of diagrams represents a situation that includes a catalyst?

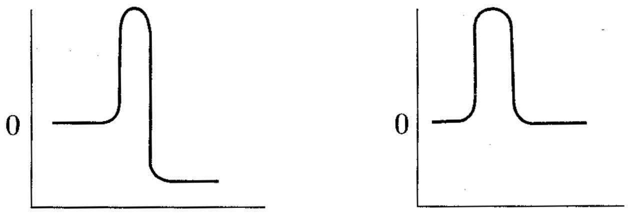
(A)



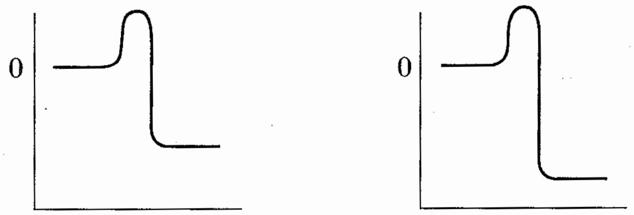
(B)



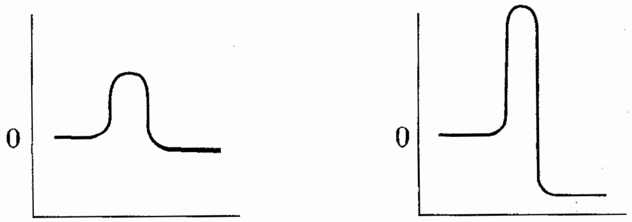
(C)



(D)

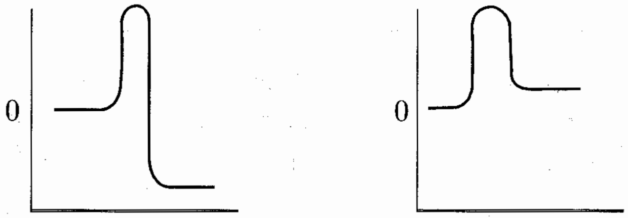


(E)

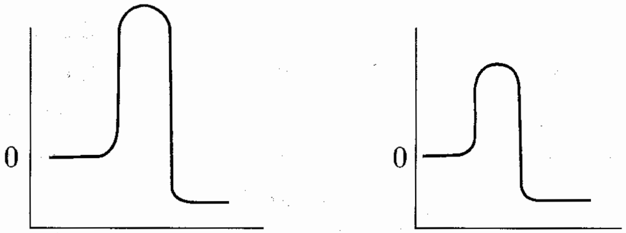


25. Which pair of potential energy/reaction coordinate diagrams represents a comparison between a reaction with high activation energy to a reaction with lower activation energy but the same heat of reaction?

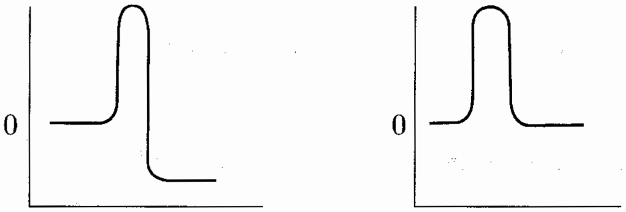
(A)



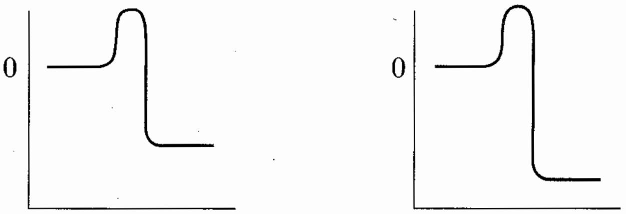
(B)



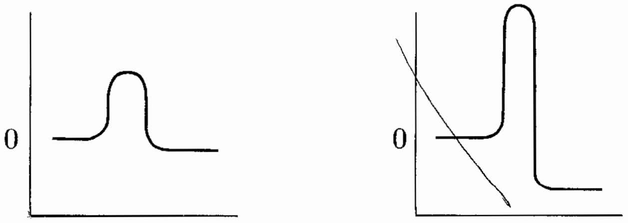
(C)



(D)



(E)



Free-Response Questions

26. $$2A_{(g)} + B_{(g)} \rightarrow C_{(g)}$$

Trial	Initial concentration mol L^{-1} [A]	Initial concentration mol L^{-1} [B]	Initial rate of formation of C mol L^{-1} sec^{-1}
I	0.40	0.20	8.0×10^{-4}
II	0.80	0.40	1.6×10^{-3}
III	0.80	0.80	3.2×10^{-3}
IV	0.60	0.60	2.4×10^{-3}
V	0.30	?	4.0×10^{-4}

(A) Write the rate law for the reaction above in the form Rate $= k[A]^x[B]^y$ including numerical values for x and y. Explain how you determined the values for exponents x and y.

(B) Calculate the specific rate constant, k. Specify the units for k.

(C) Calculate the rate of formation of C in trial IV after [A] has decreased to 0.30 M.

(D) Calculate the initial concentration of reactant B in trial V.

(E) If the temperature were raised by 10°C for any trial, what would be the effect on the initial rate of formation of C? Explain.

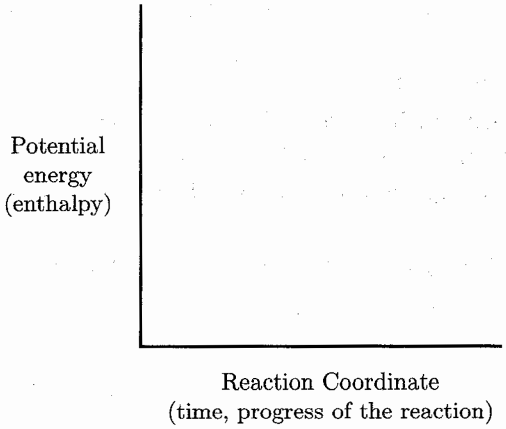
27. In the reaction below, the forward reaction is known to be first order in both PCl_3 and Cl_2. The reverse reaction is first order in PCl_5.

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)} + \text{energy}$$

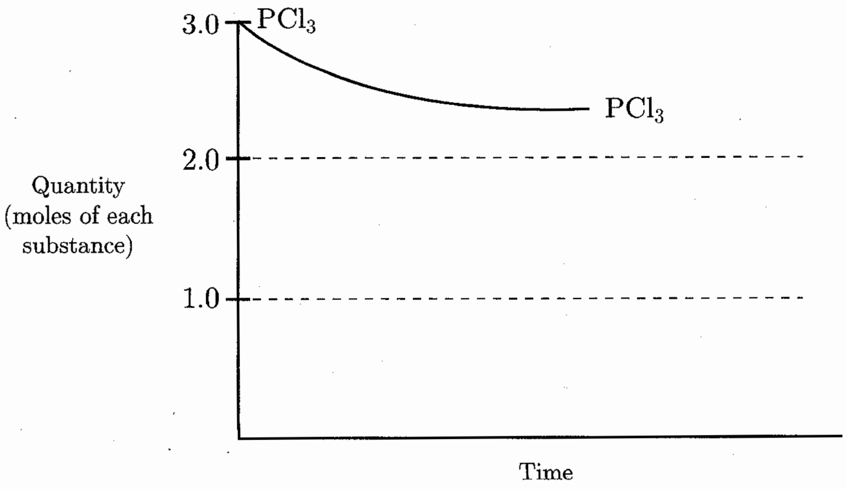
(A) Write the rate law for the forward reaction. What factors determine the numerical values of the rate constant and of each exponential term in the rate law?

(B) Propose a mechanism for the forward reaction that is based on the molecular collision theory and describe each event (elementary process) in that mechanism.

(C) On the axes provided, draw the reaction coordinate for the forward reaction that shows relative energies of components of the system. Locate and label the relative energies of the reactants, the product and the activated complex.



(D) A reaction mixture is prepared in a rigid container held at constant temperature that originally contains 3.0 moles of PCl_3 and 1.0 mole of Cl_2. On the axis provided, draw a graph that shows how the quantities of Cl_2 and PCl_5 change with time until equilibrium has been established. Equilibrium is established when the quantity of PCl_5 has become 0.60 mole. The corresponding change for PCl_3 is given. Include a separate, labeled line on your graph for each of the other two substances showing how the quantity present changes over time.



28.

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

For the exothermic reaction represented above, carried out at 298 K, the rate law is

$$\text{Rate} = k[H_2][I_2]$$

Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(A) Removal of iodine gas at constant volume and temperature.

(B) Increase in volume of the reaction vessel at constant temperature.

(C) Addition of a catalyst.
In your explanation, include a potential energy diagram with axis labeled as potential energy versus reaction coordinate for this reaction. Show a comparison between the catalyzed and non-catalyzed reactions.

(D) Increase in temperature.
In your explanation, include a diagram, showing the number of molecules as a function of energy. Use a 'before' and 'after' presentation of information to show how the temperature change affects the distribution of molecules.

(E) Increase in overall pressure by addition of argon at constant volume.

CHAPTER 7

CHEMICAL EQUILIBRIUM

Chemical equilibrium is the single most important topic on the AP exam. It gets the most ink from the question writers. As a result, it should get the most "ink" back from students. Our best advice: you should spend any available free time improving your understanding of chemical equilibrium!

WHAT IS CHEMICAL EQUILIBRIUM?

Recognizing and explaining chemical equilibrium

In Chapter 5, we discussed reactions that go to completion; that is, reactions in which the limiting reactant is consumed and a maximum quantity of product is formed. However, in actual practice, many reaction systems reach a condition in which some quantity of each reactant remains in contact with some quantity of each product and that no further change appears to occur. The system has achieved a steady state, called equilibrium, with no apparent further change in its properties including color, mass, density and pH. Any system at equilibrium is always a closed system.

Equilibrium is recognized by constant macroscopic properties explained in terms of dynamic molecular behavior. This equilibrium condition occurs as the result of two opposing reactions that are occurring at the same rate. The rate of the forward reaction is equal to the rate of the reverse reaction. The concept of molecular collisions as the basis for chemical reaction helps explain why equilibrium exists. In the very familiar Haber process

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

equilibrium is achieved when the rate of formation of ammonia is equal to the rate of consumption of ammonia.

The Reaction Quotient Experiments have shown that there is a reaction quotient (mass action expression) that describes quantitatively the contents of a reaction system which has reached equilibrium.

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]}$$

For the generalized reaction system at equilibrium $aA + bB \rightleftharpoons cC + dD$.

$$Q = K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The numerical value is known as the equilibrium constant, K_{eq}. There is a specific K_{eq} for any equilibrium system. The value of K_{eq} varies with temperature.

FACTORS AFFECTING CHEMICAL EQUILIBRIUM

Equilibrium can be disturbed when one or more of its characteristics is subjected to change.

Among the factors affecting equilibrium are

- concentration for solution systems
- volumes, concentrations or partial pressures for gas phase systems
- temperature for any system in general.

Le Chatelier's Principle By the end of the 19th Century, study of equilibrium systems was sufficiently advanced to allow the establishment of Le Chatelier's Principle, a basis for the prediction of the effects of changes in systems at equilibrium.

When a system at equilibrium is subjected to a stress, the system will shift so as to relieve the stress.

AP exam questions are often presented so that students are expected to discuss equilibrium systems and changes in those systems from one or more of three perspectives:

- rates of opposing reactions (the forward and reverse reactions)
- the equilibrium constant (or reaction quotient)
- Le Chatelier's principle

SOLVING EQUILIBRIUM PROBLEMS

Quantitative equilibrium problems

Some questions call for calculations about systems that have achieved equilibrium and systems that are moving to an equilibrium position. These questions require use of K_{eq} in a wide variety of calculations. Some commonly encountered types of equilibrium systems with examples are listed below.

Gas Phase (homogeneous) Equilibrium System

$$4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2Cl_{2(g)} \qquad K_p = \frac{P^2_{H_2O}\,P^2_{Cl_2}}{P^4_{HCl}\,P_{O_2}}$$

Gas/Solid Phases (heterogeneous) Equilibrium System - Dissociation of a Solid

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad K_p = P_{CO2}$$

Solid/solution phases (heterogeneous) - Solubility Equilibrium

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+{}_{(aq)} + CrO_{4(aq)}^{2-} \qquad K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$$

Solution phase (homogeneous) equilibrium - Ionization of a Weak Acid

$$HNO_{2(aq)} + H_2O \rightleftharpoons H_3O^+{}_{(aq)} + NO_2{}^-{}_{(aq)} \qquad K_a = \frac{[H_3O^+][NO_2{}^-]}{[HNO_2]}$$

Ionization of a Weak Base

$$CH_3NH_{2(aq)} + H_2O \rightleftharpoons CH_3NH_3{}^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_b = \frac{[CH_3NH_3{}^+][OH^-]}{[CH_3NH_2]}$$

Instability (Dissociation of a Complex Ion)

$$Ag(NH_3)_2{}^+{}_{(aq)} \rightleftharpoons Ag^+{}_{(aq)} + 2NH_{3(aq)} \qquad K_{inst} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2{}^+]}$$

Dissolving/Complex Ion Formation (Complexation)

$$Cu(OH)_{2(s)} + 4NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4{}^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$$

$$K_{diss} = \frac{[Cu(NH_3)_4{}^{2+}][OH^-]^2}{[NH_3]^4}$$

Gas/Liquid heterogeneous equilibrium (Vapor Pressure)

$$H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)} \qquad K_p = P_{H_2O}$$

Equilibrium constant expressions include only those terms whose concentrations can change such as pressures or concentrations of gases and concentrations of ions in solution.

Systems at equilibrium

For systems at equilibrium, the chemical equation is generally known, as well as enough components of the reaction quotient to permit calculation of other quantities. Solution of these problems calls for writing the equilibrium constant expression (reaction quotient or mass action expression), substituting the known quantities, then solving for the other values.

Systems moving to equilibrium

Some systems move from a previous non-equilibrium condition to a new equilibrium condition. Solution of such a problem calls for application of the principles of reaction stoichiometry to solve for concentrations at equilibrium, then further calculations using the equilibrium concentrations as determined.

One strategy commonly presented in textbooks recommends the use of a table such as that in Figure 7.1 to summarize the behavior of the system as it moves to equilibrium. Sometimes these are called "Rice", "Ice" or "Nice" tables. Especially helpful is the explicit statement of changes in quantities, Δn, *or* Δmol *due to rxn*, as the reaction proceeds. You should express all amounts in moles rather than moles per liter in order to avoid losing track of volume effects.

Figure 7.1 A Problem Solving Format for Equilibrium Problems using n_{av} Δn_{rxn} n_{av} n_{eq} $[\,]_{eq}$: an improvement on "RICE" or "ICE"

- Use this format when a reaction occurs in a system (apply principles of stoichiometry)

AND

- that system establishes a new equilibrium (apply principles of equilibrium).

Substance	A	B	C	D
n_{av}, mol available				
Δn, Δn_{rxn}, Δmol due to rxn				
n_{eq}, mol at equilibrium				
$[\,]_{eq}$, conc. at equilib.				

The Students Solution Manual has many illustrations of the use of a RICE table.

Solubility equilibrium

Solubility equilibrium can be established by dissolving the solid, usually an ionic solid, into the solvent, usually water. This is generally regarded as the forward reaction. Solubility equilibrium can also be established by mixing solutions of ions that form a precipitate, in the reverse reaction. Refer to the Ag_2CrO_4 solubility equilibrium equation above. In a typical problem, the information could be provided as mass (or moles) of the specified solute dissolved per unit volume of solvent (or solution) with directions to calculate the value for K_{sp}. Alternatively, the given information may include the K_{sp}, with the molar or mass solubility as the value to be calculated.

Acid Base equilibrium

In Chapter 9, more attention will be given to the implications of chemical equilibrium for acid/base systems that include

a. proton transfer (donation/acceptance); K_a and K_b

b. self-ionization of water; K_w

c. ionization of weak acids and bases; K_a and K_b

d. ionization of polyprotic acids; K_I, K_{II} and K_{III}

e. hydrolysis of salts; K_h

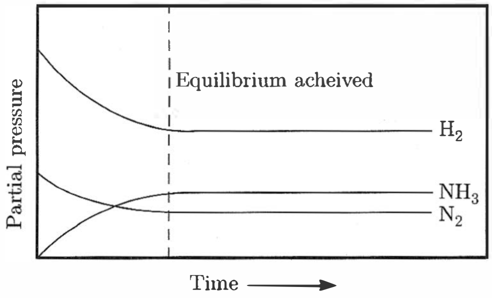
f. buffer solutions

g. titrations/pH curves

Graphic representations

Figure 7.2 shows a plot of concentration *vs* time (progress of the reaction) as a system moves from some starting conditions and achieves equilibrium after some reactants have been consumed and some products formed. Note that an unchanging horizontal line indicates the steady state characteristic of equilibrium. An abrupt vertical shift indicates a "stress" in the form of addition or removal of some portion of one or more of the reactants or products as shown in questions 21-24 below.

Figure 7.2 Establishing equilibrium



from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

III. Reactions

C. Equilibrium

1. Concept of dynamic equilibrium, physical and chemical; Le Chatelier's Principle; equilibrium constants
2. Quantitative treatment
    a. Equilibrium constants for gaseous reactions: K_p, K_c
    b. Equilibrium constants for reactions in solution
        (1) Constants for acids and bases; pK; pH
        (2) Solubility product constants and their application to precipitation and the dissolution of slightly soluble compounds
        (3) Common ion effect; buffers; hydrolysis

from the list of CHEMICAL CALCULATIONS

8. Equilibrium constants and their applications, including their use for simultaneous equilibria

from the list of EQUATIONS & CONSTANTS

$$\mathrm{Q} = \frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}} \text{ where } \mathrm{aA} + \mathrm{bB} \rightarrow \mathrm{cC} + \mathrm{dD}$$

$$K_a = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$K_b = \frac{[\mathrm{OH}^-][\mathrm{HB}^+]}{[\mathrm{B}]}$$

$$K_w = [\mathrm{OH}^+][\mathrm{H}^+] = 10^{-14} \text{ @ } 25^\circ\mathrm{C}$$

$$= K_a \times K_b$$

$$\mathrm{pH} = -\log[\mathrm{H}^+], \ \mathrm{pOH} = -\log[\mathrm{OH}^-]$$

$$14 = \mathrm{pH} + \mathrm{pOH}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$\mathrm{pOH} = \mathrm{p}K_b + \log\frac{[\mathrm{HB}^+]}{[\mathrm{B}]}$$

$$\mathrm{p}K_a = -\log K_a, \ \mathrm{p}K_b = -\log K_b$$

$$K_p = K_c(RT)^{\Delta n}, \text{where } \Delta n = \text{moles product gas} - \text{moles reactant gas}$$

from the list of RECOMMENDED EXPERIMENTS

10. Determination of the equilibrium constant for a chemical reaction

The experiment calls for measuring the changes in concentration of a colored ion in water solution using a spectrophotometer. Using Beer's Law, absorbance can be measured and corresponding concentration calculated. This is especially useful in determining the concentration of colored ions such as Cu^{2+} and Co^{3+} where those ions are precipitated from water solution to establish solubility equilibrium. The concentration of such ions can also be estimated using the unaided eye by comparing color intensity of solutions of known concentration to the color of solutions of unknown concentrations.

Multiple Choice Questions

1. For which reaction is K_c equal to K_p?

   (A) $H_{2(g)} + S_{(s)} \rightleftharpoons H_2S_{(g)}$

   (B) $2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$

   (C) $3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$

   (D) $H_{2(g)} + Br_{2(\ell)} \rightleftharpoons 2HBr_{(g)}$

   (E) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

2. Consider the reaction

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_c = 49 \text{ at } 1000\text{ K}$$

   What is the value of K_c for the reaction below?

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

   (A) $\frac{1}{49}$

   (B) $\frac{1}{7}$

   (C) $\frac{1}{(49)^2}$

   (D) 7

   (E) $(49)^2$

3. Consider the solubility equilibrium system represented by the equation below.

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

   Which occurs when $K_2SO_{4(s)}$ is added to the system at constant temperature?

   (A) $[Pb^{2+}]$ increases as the mass of $PbSO_{4(s)}$ in the system increases.

   (B) $[Pb^{2+}]$ increases as the mass of $PbSO_{4(s)}$ in the system remains the same.

   (C) $[Pb^{2+}]$ decreases as the mass of $PbSO_{4(s)}$ in the system decreases.

   (D) $[Pb^{2+}]$ decreases as the mass of $PbSO_{4(s)}$ in the system increases.

   (E) $[Pb^{2+}]$ decreases as the mass of $PbSO_{4(s)}$ in the system remains the same.

4. The K_{sp} for $PbCl_2$ is 1.6×10^{-5}. Of the following choices, which is the greatest amount of $Pb(NO_3)_{2(s)}$ that can be added to 1.0 liter of 0.010 M NaCl solution at constant temperature without causing precipitation to occur? (Assume no change in volume.)

   (A) 4.0×10^{-4} mol
   (B) 1.5×10^{-3} mol
   (C) 8.0×10^{-3} mol
   (D) 4.0×10^{-2} mol
   (E) 1.5×10^{-1} mol

Questions 5-9:

$$4H_{2(g)} + CS_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2S_{(g)}$$

The system below reaches equilibrium according to the equation above. A mixture of 2.50 mol $H_{2(g)}$, 1.50 mol $CS_{2(g)}$, 1.50 mol $CH_{4(g)}$ and 2.00 mol $H_2S_{(g)}$ is placed in a 5.0 L rigid reaction vessel. When equilibrium is achieved, the concentration of $CH_{4(g)}$ has become 0.25 mol L^{-1}. The five questions below apply to this equilibrium system.

(You may use the tabular format below to help you analyze this problem. It is unlikely that this format will appear on the examination. However, its use will help you work through some quantitative principles of chemical equilibrium. Values printed in the table are those given in the problem.)

	$H_{2(g)}$	$CS_{2(g)}$	$CH_{4(g)}$	$H_2S_{(g)}$
mol available	2.50	1.50	1.50	2.00
mol change				
mol at equilibrium				
concentration mol L^{-1}			0.25	

5. Changes in concentration occur as this system approaches equilibrium. Which expression gives the best comparison of the changes in those concentrations shown in the ratio below?

$$\frac{\Delta[H_2S]}{\Delta[CS_2]}$$

   (A) $\frac{+2}{+1}$

   (B) $\frac{+2}{-1}$

   (C) $\frac{-2}{+1}$

   (D) $\frac{-1}{+1}$

   (E) $\frac{-1}{+2}$

6. What is the change in the number of moles of $H_2S_{(g)}$ present as the system moves from its original state to the equilibrium described?

(A) −1.25
(B) −0.50
(C) −0.25
(D) +0.25
(E) +0.50

7. What is the number of moles of $CS_{2(g)}$ at equilibrium?

(A) 0.25
(B) 0.35
(C) 0.75
(D) 1.25
(E) 1.75

8. What is the concentration in moles per liter of $H_{2(g)}$ at equilibrium?

(A) 0.50
(B) 0.70
(C) 1.0
(D) 2.0
(E) 3.0

9. Which correctly describes the values for ΔG, the free energy change, and Q, the mass action expression (reaction quotient), when the mixture was prepared?

(A) $\Delta G = 0$, $Q = K_{eq}$
(B) $\Delta G > 0$, $Q < K_{eq}$
(C) $\Delta G > 0$, $Q > K_{eq}$
(D) $\Delta G < 0$, $Q > K_{eq}$
(E) $\Delta G < 0$, $Q < K_{eq}$

Questions 10–13:

$$\text{heat} + N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

Consider an equilibrium system based on the reaction above. This equilibrium mixture is contained in a piston.

10. Which occurs when the volume of the system is increased at constant temperature?

	number of molecules of NO_2	**total number of molecules of all gases**	**K_p**
(A)	increases	decreases	remains the same
(B)	increases	remains the same	remains the same
(C)	increases	increases	remains the same
(D)	remains the same	decreases	decreases
(E)	remains the same	increases	decreases

11. Which occurs when the force on the piston is decreased at constant temperature?

	partial pressure of N_2O_4	**total pressure of of all gases**	**K_p**
(A)	decreases	increases	remains the same
(B)	increases	decreases	remains the same
(C)	decreases	decreases	remains the same
(D)	increases	decreases	decreases
(E)	increases	increases	decreases

12. Which occurs when the temperature of the system is increased at constant volume?

	number of molecules of N_2O_4	**total number of molecules of all gases**	**K_p**
(A)	increases	decreases	remains the same
(B)	decreases	increases	remains the same
(C)	increases	decreases	increases
(D)	decreases	decreases	increases
(E)	decreases	increases	increases

13. Which occurs when $NO_{2(g)}$ is added to the system at constant volume and temperature?

	number of molecules of N_2O_4	**total number of molecules of all gases**	**K_P**
(A)	increases	decreases	remains the same
(B)	increases	increases	remains the same
(C)	decreases	increases	remains the same
(D)	decreases	decreases	decreases
(E)	increases	increases	decreases

14. $$HgO_{(s)} + 4I^-_{(aq)} + H_2O \rightleftharpoons HgI_4{}^{2-}{}_{(aq)} + 2OH^-_{(aq)}$$

Consider the equilibrium above. Which of the following changes will increase the concentration of $HgI_4{}^{2-}{}_{(aq)}$?

I. adding 6*M* HNO_3
II. increasing mass of $HgO_{(s)}$ present
III. adding $KI_{(s)}$

(A) II only
(B) III only
(C) I and III only
(D) II and III only
(E) I, II, and III

15. The molar solubility of Ag_2CrO_4 is 1.3×10^{-4} at 25°C. Which expression gives the value for the solubility product constant, K_{sp}, for Ag_2CrO_4?

(A) $(1.3 \times 10^{-4})^2$

(B) $(1.3 \times 10^{-4})^3$

(C) $(2.6 \times 10^{-4})(1.3 \times 10^{-4})$

(D) $(2.6 \times 10^{-4})^2(1.3 \times 10^{-4})$

(E) $\dfrac{(2.6 \times 10^{-4})^2}{(1.3 \times 10^{-4})}$

Questions 16–19:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92 \text{ kJ}$$

The four questions below apply to an equilibrium system based on the reversible reaction given above.

16. When the temperature of such an equilibrium system is increased at constant volume, which property is least affected?

(A) density
(B) pressure
(C) concentration of $NH_{3(g)}$
(D) concentration of $N_{2(g)}$
(E) average kinetic energy

17. How are the rates of the opposing reactions and the value of the equilibrium constant, K_p, affected when heat is added to this system?

(A) The reaction rates remain unchanged and K_p decreases.
(B) The forward reaction will be favored and K_p decreases.
(C) The forward reaction will be favored and K_p increases.
(D) The reverse reaction will be favored and K_p decreases.
(E) The reverse reaction will be favored and K_p increases.

18. Which observation confirms the fact that equilibrium has been reached in such a system confined in a closed, rigid container?

(A) The density remains constant.
(B) The odor of ammonia can first be detected.
(C) The pressure is decreasing at a constant rate.
(D) The partial pressure of hydrogen remains constant.
(E) The mass of the system has decreased to a constant value.

19. Which occurs when such an equilibrium system is subjected to a stress by the addition of $H_{2(g)}$ and the system proceeds to a new equilibrium?

I. Heat will be released.
II. Some of the added $H_{2(g)}$ will be consumed.
III. Some of the $N_{2(g)}$ present originally will be consumed.

(A) II only
(B) III only
(C) I and III only
(D) II and III only
(E) I, II, and III

20. Consider the equilibrium system

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)} + \text{heat}$$

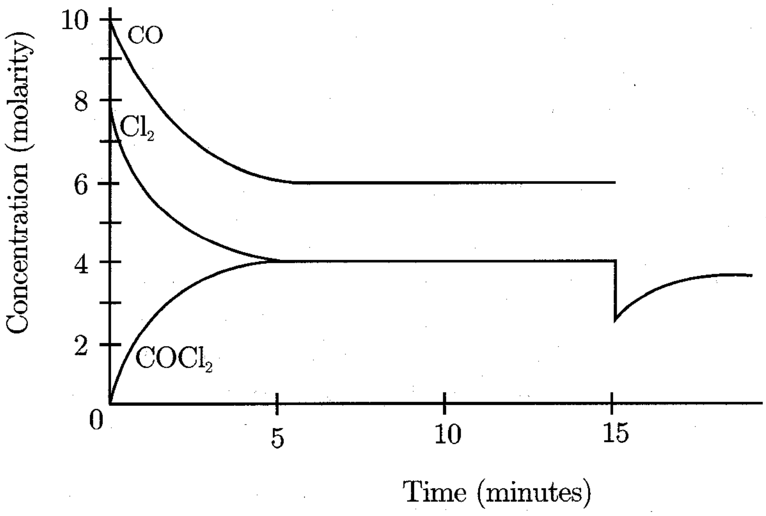
What is the effect on the rates of the opposing reactions when the temperature of this system is increased?

(A) The $\text{rate}_{\text{forward}}$ increases; the $\text{rate}_{\text{reverse}}$ decreases.
(B) The $\text{rate}_{\text{forward}}$ decreases; the $\text{rate}_{\text{reverse}}$ decreases.
(C) The $\text{rate}_{\text{forward}}$ increases; the $\text{rate}_{\text{reverse}}$ remains the same.
(D) The $\text{rate}_{\text{forward}}$ remains the same; the $\text{rate}_{\text{reverse}}$ decreases.
(E) Both $\text{rate}_{\text{forward}}$ and $\text{rate}_{\text{reverse}}$ increase.

Questions 21-24: Consider the reaction

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)} + \text{heat}$$

A system is established in which the original concentration of CO is 10.0 *M* and that of Cl_2 is 8.0 *M*. The system is contained in a sealed rigid container. The progress of the reaction is given in the graph below. The system is maintained at constant temperature.



21. Which is the best comparison of Q, the reaction quotient, to K_c, the equilibrium constant, at time 2.5 minutes?

(A) $Q > 0$ and $Q > K_c$
(B) $Q > 0$ and $Q = K_c$
(C) $Q > 0$ and $Q < K_c$
(D) $Q < 0$ and $Q > K_c$
(E) $Q < 0$ and $Q < K_c$

22. Which is the best description of the rate of the forward reaction, $\text{Rate}_{\text{forward}}$, between time 0 and time 4 minutes?

(A) $\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$ and decreasing
(B) $\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$ and increasing
(C) $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$ and constant
(D) $\text{Rate}_{\text{forward}} < \text{Rate}_{\text{reverse}}$ and decreasing
(E) $\text{Rate}_{\text{forward}} < \text{Rate}_{\text{reverse}}$ and increasing

23. Which is the best explanation of the cause of the changes in concentration that occur after time 15 minutes?

(A) increase in temperature
(B) decrease in temperature
(C) addition of a suitable catalyst
(D) addition of some $COCl_2$
(E) removal of some $COCl_2$

24. Which is the best comparison of the

- rate of the forward reaction at 10 minutes, $\text{Rate}_{\text{forward,10 min}}$

  and the

- concentration of CO at 10 minutes, $[CO]_{10\text{ min}}$, the first equilibrium

  to the

- corresponding characteristics at 20 minutes, when the second equilibrium is established

(A) $\text{Rate}_{\text{forward,10min}} = \text{Rate}_{\text{forward,20min}}$; with $[CO]_{10\text{ min}} = [CO]_{20\text{ min}}$
(B) $\text{Rate}_{\text{forward,10min}} < \text{Rate}_{\text{forward,20min}}$; with $[CO]_{10\text{ min}} = [CO]_{20\text{ min}}$
(C) $\text{Rate}_{\text{forward,10min}} > \text{Rate}_{\text{forward,20min}}$; with $[CO]_{10\text{ min}} = [CO]_{20\text{ min}}$
(D) $\text{Rate}_{\text{forward,10min}} < \text{Rate}_{\text{forward,20min}}$; with $[CO]_{10\text{ min}} > [CO]_{20\text{ min}}$
(E) $\text{Rate}_{\text{forward,10min}} > \text{Rate}_{\text{forward,20min}}$; with $[CO]_{10\text{ min}} > [CO]_{20\text{ min}}$

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25. Calcium fluoride, CaF_2, is a nearly insoluble salt with $K_{sp} = 3.9 \times 10^{-11}$ at 298 K. Addition of which substance is most likely to increase the solubility of CaF_2 at constant temperature?

(A) $NaF_{(s)}$
(B) $CaCl_{2(s)}$
(C) $HCl_{(aq)}$
(D) H_2O
(E) $C_2H_5OH_{(\ell)}$

Free-Response Questions

26. $$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_p = 630 \text{ at } 546\text{ K}$$

A system is prepared by placing equimolar amounts of the three gases shown in the equation above in a suitable rigid container held at constant volume. Equilibrium is established at 546 K.

(A) When equilibrium is established, how does $[PCl_3]$ compare to $[Cl_2]$? Explain.

(B) When equilibrium is established, how does $[PCl_5]$ compare to $[PCl_3]$? Explain.

(C) When equilibrium is established, how does the rate of the forward reaction compare to the rate of the reverse reaction? Explain.

(D) If the volume of the container is increased at constant temperature of 546 K, the equilibrium is disrupted.

(1) What effect is observed on the number of moles of $PCl_{5(g)}$ in the system? Explain.

(2) Does the value of K_p increase, decrease or remain the same? Explain.

27. Calcium sulfate, $CaSO_4$ (molar mass: 136 g), is a nearly insoluble salt with a solubility product constant, K_{sp}, of 2.4×10^{-5}.

(A) Write the chemical equation for the solubility equilibrium of calcium sulfate.

(B) Calculate the solubility of calcium sulfate in grams solute per 100 grams of solvent. Assume that the volume occupied by the solute in the solution is negligibly small.

(C) Does precipitation occur when 100. mL of 0.050 *M* $CaCl_{2(aq)}$ is added to 100. mL of 0.10 *M* $K_2SO_{4(aq)}$? Show calculations to support your response.

(D) In another experiment, 100. mL of 0.020 *M* $CaCl_{2(aq)}$ is added to 200. mL of 0.20 *M* $K_2SO_{4(aq)}$. Calculate the equilibrium concentrations of $Ca^{2+}{}_{(aq)}$ and $SO_4{}^{2-}{}_{(aq)}$.

28. A system is prepared by placing 2.00 mol $H_{2(g)}$ and 3.00 mol $I_{2(g)}$ in a 3.00 L container at 700. K. The system reaches equilibrium according to the equation

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

The number of moles of $HI_{(g)}$ at equilibrium is 1.90.

(A) Write the equilibrium expression, K_c, for this system.

(B) Calculate the value for K_c.

(C) Calculate the partial pressure in atmosphere of $I_{2(g)}$ at equilibrium.

(D) If the system were changed by adding 1.00 mol $H_{2(g)}$, what would be the partial pressure of $HI_{(g)}$ at the new equilibrium?

CHAPTER 8

THERMODYNAMICS

Another major topic for the Advanced Placement Chemistry examination is that of thermodynamics. You should be familiar with problems that trace heat flow (enthalpy). You should also understand the role of entropy and entropy changes, as well as the trend in the universe towards increasing disorder. Changes in enthalpy and entropy are linked in the Gibbs Free Energy equation which helps identify spontaneous processes.

THERMODYNAMICS – THREE LAWS

Thermodynamics is the study of energy and how it can be expressed as heat or work. The **First Law of Thermodynamics** states that the amount energy in the universe is a finite quantity and that it cannot be created nor destroyed. It can be expressed as either heat or as work. In chemistry, we frequently assume that no work is being performed (since ions or molecules in solution do not exert a force over a distance). You can track energy changes by observing only heat flow **(changes in enthalpy)** in relation to chemical reactions. In this branch of thermodynamics, called **thermochemistry**, you usually make measurements of heat flow using a **calorimeter**. The **coffee cup calorimeter** is made by stacking together several cups made of expanded polystyrene (hence the tradename "Styrofoam"). Any reaction that occurs in a solution contained within this well-insulated container is assumed to retain all heat that is produced. No heat is exchanged with the immediate surroundings. It is also assumed that any reaction occurs at constant pressure. While these assumptions may not always be true, they are frequently close enough to allow making reasonable temperature measurements and corresponding heat flow calculations. If a constant volume, variable pressure situation is to be studied, a **bomb calorimeter** can be used instead. For this device, the heat absorbed by the calorimeter and its contents is carefully measured and factored into any calculations. **Hess's Law** allows you to predict the enthalpy changes of a reaction by combining any plausible (or measurable) set of equations for chemical reactions that lead to the net reaction under consideration. The enthalpy changes, ΔH, for these component reactions are obtained from a reference source or measured in the laboratory, then combined algebraically. You can use this method because enthalpy is a **state function**, a characteristic whose value is independent of the pathway followed to reach it.

The **Second Law of Thermodynamics** specifies that in any spontaneous process, the entropy S (or disorder) of the universe increases. The effect of **entropy** changes on chemical reactions is much more subtle than that of enthalpy changes, yet it can have a measurable effect in certain circumstances as noted in the equation that defines **Gibbs Free Energy** change, $\Delta G = \Delta H - T\Delta S$. Calculation of ΔG permits prediction of direction of progress for a chemical reaction; that is, whether or not a reaction is spontaneous. A negative value for ΔG indicates a spontaneous reaction, or that the forward reaction is favored. A positive value predicts a non-spontaneous forward reaction, or that the reverse reaction is spontaneous. A value of zero indicates that the forward reaction is as favorable as the reverse reaction, or that an equilibrium position has been attained.

The **Third Law of Thermodynamics** includes a definition that establishes a baseline for entropy values. The entropy of a perfectly aligned solid crystal at zero kelvins (K) is assumed to be zero since there can be no situation more ordered.

VOCABULARY: THERMODYNAMICS

The Three Laws of Thermodynamics

First Law of Thermodynamics	energy cannot be created nor destroyed, just transferred - energy in the universe is conserved: E(energy) = Q(heat) + W(work)
Second Law of Thermodynamics	the total entropy of the universe increases in a spontaneous process; entropy is always increasing in the universe
Third Law of Thermodynamics	a pure, perfect crystal at 0 kelvins has zero entropy
spontaneous	the direction a process will take, if left alone and given sufficient time; indicated by sign of ΔG value; spontaneity is a state function
entropy (S)	the quantitative measure of disorder or randomness, influenced by temperature and position of reacting particles; $\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}}$ $\Delta G = \Delta H - T\Delta S$ At equilibrium $\Delta G = 0$, therefore $\Delta S = \Delta H/T$
standard thermodynamic conditions	298 K, 1 atm, 1 *M*
free energy change (ΔG)	the part of a system's energy that is ordered and available to become spontaneously disordered; the balance struck between the tendency toward minimum energy and the tendency toward maximum disorder

Functions and Systems

state function	function or property whose value depends only on the present state of the system, not on the path used to arrive at the condition.
path function	function that depends upon how the change occurs; not frequently addressed in AP chemistry
system	the material(s) and their changes being studied and measured
open system	both matter and energy can be exchanged between system and surroundings
closed system	energy can be exchanged between components of the system, only; no exchange of matter
isolated or insulated system	neither energy nor matter can be exchanged

Temperature, Heat and Work

temperature	a measure of the average kinetic energy associated with molecular motion
heat (Q)	transfer of thermal energy between a system and its surroundings, flows from hot to cold
molar heat capacity (C_p)	amount of heat energy required to raise the temperature of one mole of substance by one degree Celsius at constant pressure
work	energy used to move an object against an opposing force
pressure	force/unit area; measured in kPa, atm, torr, or mmHg
Enthalpy change (ΔH)	heat (energy change) for a process under constant pressure conditions; predict ΔH for a reaction by using standard heats of formation or bond energies. $\Delta H^\circ = \sum \Delta H^\circ_{f\text{, products}} - \sum \Delta H^\circ_{f\text{, reactants}}$ $\Delta H_{rx} = \sum \text{bonds broken} - \sum \text{bonds formed}$
Hess's Law of Heat of Summation	the enthalpy change for any process is equal to the sum of the enthalpy changes for any set of steps that leads from the initial to final condition of the process; $\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3$
Energy unit	1 joule (J) $=$ 1 kg m^2/sec^2 (as in $\frac{1}{2}mv^2$) 4.18 J $=$ 1 calorie $=$ the amount of heat needed to raise the temperature of one gram of water by one degree Celsius
Heat (energy flow)	$Q = m\ c\ \Delta T$ describes the energy flow within a substance as heat, where m = mass of substance; c = specific heat capacity of the substance; ΔT = change in temperature
calorimeter	an isolated system calibrated prior to use to determine its heat capacity; Q lost by rx = Q gained by reaction system + Q gained by calorimeter $= mc\Delta T + C_{cal}\Delta T$

Changes in Work and Enthalpy

ΔH – change in enthalpy

Endothermic – describes a system which absorbs heat energy; ΔH (+); $\Delta H > 0$

Exothermic – describes a system which releases heat energy; ΔH (−); $\Delta H < 0$

Work including Δ(PV) work as energy

(+) Work performed on a chemical reaction system from the universe; "endoworkic", a concept parallel to endothermic; eg W or $\Delta(PV)(+)$; W or $\Delta(PV) > 0$

(−) Work performed by a chemical reaction system against the universe; "exoworkic" a concept parallel to exothermic; e.g. burning a fuel; W or $\Delta(PV)(-)$; W or $\Delta(PV) < 0$

$$W = P_{ext}\Delta V$$

Indications of Increasing Entropy

1. For progression through the phases of matter, entropy increases; (s) < (ℓ) < (g). Gases are clearly more disordered than liquids or solids.
2. In the dissolving process, solutions become more entropic as solid or liquid solute is dispersed in a liquid solvent. When a gas solute dissolves in a liquid solvent, entropy decreases. The system becomes more ordered.
3. Entropy increases with increasing mass and increasing numbers of particles since there are more positions possible for atoms or electrons.
4. Entropy increases with increasing delocalization of electrons. Ionic bonds are formed due to transfer of electrons which are then permanently localized to one nucleus. In covalent bonds, electrons are shared between two nuclei. In metallic bonds, electrons are shared among nuclei. Entropy increases from ionic to covalent to metallic bonds in terms of delocalization of electrons.
5. Increasing entropy ($\Delta S > 0$) is associated with weaker bonds and increasing softness.
6. Entropy increases with chemical complexity. For example, consider the trend in entropy values from NaCl (72.33 J mol^{-1} K^{-1}) to $MgCl_2$ (89.0) to $AlCl_3$ (109.3).

Gibbs Free Energy

$\Delta G < 0$ (negative) means spontaneous (forward) reaction

$\Delta G > 0$ (positive) means non-spontaneous (forward) reaction

$\Delta G = \Delta H - T\Delta S$

for indicated combinations of values of ΔH and ΔS respectively

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

where ° refers to the standard conditions of 1 atm and 298 K.

Note: ΔG° is read as *delta gee zero*, *delta gee naught* or even *delta gee halo*)

How changes in enthalpy and entropy affect Gibbs Free Energy change

Some nonspontaneous endothermic reactions become spontaneous at a sufficiently elevated temperature, for example, boiling water at 100 °C and 1 atm.

Similarly, some exothermic reactions become nonspontaneous at a sufficiently elevated temperature, for example, freezing water at 0°C and 1 atm. See Figure 8.1 for a quick summary of these thermodynamic parameters.

Figure 8.1 Thermodynamic parameters

ΔH	ΔS	ΔG for the process under consideration
(−)	(+)	Spontaneous at any temperature
(+)	(+)	Endothermic non-spontaneous reactions become spontaneous at sufficiently high temperature
(−)	(−)	Exothermic spontaneous reactions become non-spontaneous at sufficiently high temperature
(+)	(−)	Non-spontaneous at any temperature

Linking Thermodynamics, Equilibrium and Electrochemistry

A spontaneous reaction is indicated by a negative value for $\Delta G°$, a positive voltage, $E°$, and a positive exponent for a K_{eq} value.

$$\text{The quantitative link: } \Delta G° = -R\,T \ln K_{eq} = -n\Im E°$$

See Fig. 8.2 for a quick summary of spontaneity and its relation to ΔH and ΔS.

Figure 8.2 Summary of Thermodynamic terms

Term	**Symbol**	**What it measures**	**Interpretation**
Enthalpy change	ΔH	heat flow	− = exothermic + = endothermic
Entropy change	ΔS	disorder	− = increase in disorder + = decrease in disorder
Gibbs Free Energy change	ΔG	spontaneity	− = process will occur + = process will not occur

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

III. Reactions

E. Thermodynamics

1. State functions
2. First law: change in enthalpy; heat of formation; heat of reaction; Hess's law; heats of vaporization and fusion; calorimetry
3. Second law: entropy; free energy of formation; free energy of reaction; dependence of change in free energy on enthalpy and entropy changes
4. Relationship of change in free energy to equilibrium constants and electrode potentials

from the list of CHEMICAL CALCULATIONS

10. Thermodynamic and thermochemical calculations

from the list of EQUATIONS & CONSTANTS

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta H^\circ = \sum \Delta H^\circ_{f\ \text{products}} - \sum \Delta H^\circ_{f\ \text{reactants}}$$

$$\Delta G^\circ = \sum \Delta G^\circ_{f\ \text{products}} - \sum \Delta G^\circ_{f\ \text{reactants}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ \ln K = -2.303RT\ \log K = -n\Im E^\circ$$

$$q = mc\Delta T$$

$$C_p = \Delta H/\Delta T$$

c = specific heat capacity, T = temperature, K = equilibrium constant,

V = volume

from the list of RECOMMENDED EXPERIMENTS

13. Determination of enthalpy change associated with a reaction

Multiple Choice Questions

Questions 1-5: The set of lettered choices is a list of symbols used in thermodynamics and thermochemistry. Select the one lettered choice that best fits each numbered statement. A choice may be used once, more than once or not at all.

(A) K_c
(B) ΔG
(C) ΔH
(D) ΔS
(E) E_a

1. Its value is negative for any exothermic reaction.

2. Its value is negative for any spontaneous reaction.

3. Its value is calculated using the absolute (Kelvin) temperature and two of the other choices in the set.

4. Its value represents the change in randomness as a reaction proceeds.

5. Its value is determined by using molar concentrations at equilibrium in the mass action expression.

Questions 6-8: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H° = -92$ kJ

The Haber process is a commercial method for the manufacture of ammonia. It is based upon the equilibrium shown in the equation above. The absolute standard entropies, S°, of the components of this system are given below.

$$S^\circ_{N_2} = 192\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$S^\circ_{H_2} = 131\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$S^\circ_{NH_3} = 193\ \text{J K}^{-1}\ \text{mol}^{-1}$$

6. The value of $\Delta S°$ in J K^{-1} for the reaction above is closest to

(A) +200
(B) +100
(C) 0
(D) −100
(E) −200

7. Which interval includes ΔG for this reaction at 200 K, assuming ΔS and ΔH are constant over a wide range of temperatures?

   (A) less than −100 kJ
   (B) between −100 and −40 kJ
   (C) between −40 and +40 kJ
   (D) between −40 and +100 kJ
   (E) greater than +100 kJ

8. Which describes the change in ΔG and the change in spontaneity of the reaction as the temperature increases to values above 460 K?

   (A) ΔG increases to zero and the reaction achieves equilibrium.
   (B) ΔG decreases to values less than zero and the reaction becomes spontaneous.
   (C) ΔG decreases to values less than zero and the reaction becomes non-spontaneous.
   (D) ΔG increases to values greater than zero and the reaction becomes spontaneous.
   (E) ΔG increases to values greater than zero and the reaction becomes non-spontaneous.

---

9. The molar heat of fusion, ΔH_{fus}, for water is 6.01 kJ mol^{-1}. Which expression gives the molar entropy of fusion, ΔS_{fus}, in kJ K^{-1} mol^{-1} for ice at its normal melting point?

   (A) $\frac{6.01}{273}$
   (B) $\frac{6.01}{298}$
   (C) 6.01×4.18
   (D) 6.01×273
   (E) 6.01×298

10. The molar heat of fusion, ΔH_{fus}, for water is 6.01 kJ mol^{-1}. The specific heat capacity for water, C_p, is 75 J mol^{-1} $°C^{-1}$. Which expression gives the quantity of energy needed to change 1.0 mol ice at 0°C to liquid water at 25°C?

   (A) $\frac{6010}{75 \times 25}$
   (B) $6.01 + 75$
   (C) $6010 + (75 \times 25)$
   (D) $\frac{6010}{298} + (75 \times 25)$
   (E) $\frac{6010 + (75 \times 25)}{298}$

11. The heat of neutralization for a strong acid in dilute water solution is about 60 kJ mol^{-1}. What quantity of heat in kJ is produced when 100. mL of 1.0 *M* H_2SO_4 is mixed with 100. mL of 1.0 *M* KOH?

(A) 0.10
(B) 0.30
(C) 0.40
(D) 6.0
(E) 18

12. Which reaction illustrates the least increase in entropy?

(A) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
(B) $C_6H_{6(\ell)} \rightarrow C_6H_{6(g)}$
(C) $2KClO_{3(s)} \rightarrow 3O_{2(g)} + 2KCl_{(s)}$
(D) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
(E) $C_2H_5OH_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

13. For which reaction is ΔH most nearly equal to ΔE?

(A) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$
(B) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
(C) $C_2H_5OH_{(\ell)} \rightarrow C_2H_5OH_{(g)}$
(D) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
(E) $BaO_{2(s)} \rightarrow BaO_{(s)} + \frac{1}{2}O_{2(g)}$

14. Which equation represents the standard formation reaction for $BaSO_{4(s)}$ at 298 K?

(A) $BaS_{(s)} + 2O_{2(g)} \rightarrow BaSO_{4(s)}$
(B) $Ba_{(s)} + \frac{1}{8}S_{8(s)} + 2O_{2(g)} \rightarrow BaSO_{4(s)}$
(C) $Ba_{(s)} + S_{(s)} + 4O_{(g)} \rightarrow BaSO_{4(s)}$
(D) $Ba^{2+}{}_{(aq)} + S^{6+}{}_{(aq)} + 4O^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}$
(E) $Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}$

15. Which describes the thermodynamic parameters for the system below at 298 K and one atm?

$$H_2O_{(g)} \rightleftharpoons H_2O_{(\ell)}$$

	ΔG	ΔH	ΔS
(A)	0	> 0	> 0
(B)	0	> 0	< 0
(C)	< 0	> 0	< 0
(D)	< 0	< 0	< 0
(E)	< 0	< 0	> 0

16. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(\ell)}$ $\Delta H° = -889$ kJ

$$\Delta H_f^\circ \text{ for } H_2O_{(\ell)} = -286 \text{ kJ mol}^{-1}$$
$$\Delta H_f^\circ \text{ for } CO_{2(g)} = -393 \text{ kJ mol}^{-1}$$

Which expression gives the standard heat of formation, ΔH_f°, for methane, CH_4, in kJ mol^{-1} based on the data above?

(A) $-889 + 2(286) + 393 + 2(32)$
(B) $889 - 2(286) - 393 - 2(32)$
(C) $-889 + 2(286) + 393$
(D) $889 + 2(286) + 393$
(E) $889 - 2(286) - 393$

17. A cube of ice is added to some hot water in an insulated container which is then sealed. There is no heat exchange with the surroundings. Which describes the system once it has shifted to a new equilibrium?

I. The average kinetic energy of the liquid phase has decreased.
II. The total energy of the system has decreased.
III. The entropy of the system has increased.

(A) I only
(B) III only
(C) I and II only
(D) I and III only
(E) I, II, and III

18. One version of the First Law of Thermodynamics is expressed as

$$\Delta E = q + w$$

Which gives the sign convention for this relationship that is usually used in chemistry?

	heat, q added to the system	**heat, q added to the surroundings**	**work, w done on the system**	**work, w done on the surroundings**
(A)	−	+	−	−
(B)	+	+	+	+
(C)	+	+	+	−
(D)	+	−	+	−
(E)	+	−	−	−

19. $$C_2H_5OH_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

At 298 K, the change in enthalpy, ΔH, for the reaction above is given by

(A) $\Delta E + RT$
(B) $\Delta E - 2RT$
(C) $\Delta E + 2RT$
(D) $5RT - \Delta E$
(E) $2RT - \Delta E$

20. Which applies to any reaction that proceeds spontaneously to form products from initial standard state conditions?

I. $\Delta G < 0$
II. $K_{eq} > 1$
III. $\Delta H < 0$

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

21.

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	$\Delta H^\circ_{comb} = -394$ kJ
$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$	$\Delta H^\circ_{comb} = -286$ kJ
$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(\ell)}$	$\Delta H^\circ_{comb} = -2{,}222$ kJ
$3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$	$\Delta H^\circ_f =$

Using values above, which expression gives the heat of formation, $\Delta H_f{}^\circ$, for propane, C_3H_8?

(A) $-2{,}222 + [394 - 286]$
(B) $2{,}222 - 394 - 286$
(C) $-2{,}222 + [-3(394) - 4(286)]$
(D) $-2{,}222 + [3(394) + 4(286)]$
(E) $2{,}222 + [3(-394) + 4(-286)]$

22. $$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)}$$

The reaction above is not spontaneous at any temperature. Which applies to the system at 298 K?

	ΔG	ΔH	ΔS
(A)	+	+	+
(B)	+	+	−
(C)	−	+	+
(D)	−	−	−
(E)	−	−	+

23. Which applies to any reaction that has negative values for both ΔH and ΔS?

I. The reaction is spontaneous at all temperatures.
II. The reaction is exothermic.
III. ΔG increases (becomes more positive) as temperature increases.

(A) I only
(B) III only
(C) I and III only
(D) II and III only
(E) I, II, and III

24. For a given reaction, the values for standard free energy change, ΔG°, and the equilibrium constant, K_{eq}, are both measures of the extent to which a reaction proceeds. Which is a reasonable value for ΔG° in kJ mol^{-1} when the corresponding value for $K_{eq} = 6.9 \times 10^5$ at 298 K?

(A) −100
(B) −30
(C) 0
(D) +30
(E) +100

25. One version of the Second Law of Thermodynamics for any spontaneous process includes the statement

$$\Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0$$

Which is the best interpretation of this statement?

(A) For any spontaneous process, the entropy of the universe increases.
(B) For any spontaneous process, the free energy change is negative.
(C) For any spontaneous process, the entropy change for the system is positive.
(D) For any spontaneous process, the entropy change for the system is less than the entropy change for the surroundings.
(E) For any spontaneous process, the entropy change for the system is greater than the entropy change for the surroundings.

Free-Response Questions

26. The Gibbs Free Energy change, ΔG, describes the spontaneity of a chemical change in terms of temperature and changes in enthalpy and entropy terms, as affected by temperature.

    (A) What is the value of ΔG for any reaction system at equilibrium?

    (B) What is the sign of ΔG for any reaction that is spontaneous?

    (C) What are the signs of ΔH and ΔS for each of the reaction circumstances described under the following situations? Explain.

    (1) spontaneous regardless of temperature
    (2) spontaneous at low temperatures but non-spontaneous at high temperatures
    (3) spontaneous at high temperatures but non-spontaneous at low temperatures
    (4) non-spontaneous regardless of temperature

27. The compound $BrCl_{(g)}$ is produced by mixing bromine gas and chlorine gas at 298 K. The mixture reaches equilibrium in a very short time.

$$Br_{2(g)} + Cl_{2(g)} \rightleftharpoons 2BrCl_{(g)}$$

	ΔH_f°, kJ mol^{-1}	**ΔG_f°, kJ mol^{-1}**	**S°, J mol^{-1} K^{-1}**
$Br_{2(g)}$	30.7	3.14	152.2
$BrCl_{(g)}$	14.7	−0.88	239.7
$Cl_{2(g)}$	0	0	222.8

(A) What is the standard enthalpy of reaction, ΔH°, in kJ at 298 K, for the reaction between $Br_{2(g)}$ and $Cl_{2(g)}$ as shown above?

(B) What is the numerical value of the standard entropy change, ΔS°, at 298 K for this reaction? Include units.

(C) What is the numerical value of the standard entropy change of formation, ΔS_f°, for $BrCl_{(g)}$ at 298 K? Include units.

(D) What is the numerical value of the equilibrium constant, K_p, for this reaction at 298 K?

28.

	ΔH_f°, (kJ mol^{-1})	ΔG_f°, kJ mol^{-1}	S°, J mol^{-1} K^{-1}
$CO_{2(g)}$	−393.5	−394.4	213.6
$C_{(s)}$	0	0	5.69
$H_{2(g)}$	0	0	130.58
$H_2O_{(\ell)}$	−285.83	−236.81	69.96
$O_{2(g)}$	0	0	205.0
$C_6H_{12}O_{6(s)}$	−1,273.02	?	212.1

All values taken at 298 K.

(A) Write a balanced equation for the formation of glucose, $C_6H_{12}O_{6(s)}$, from its elements. Include the symbol for the phase of each reactant and product in its standard state.

(B) Calculate the standard entropy change of formation, ΔS_f°, for glucose, $C_6H_{12}O_{6(s)}$ at 298 K. Specify units.

(C) Calculate the standard free energy change of formation, ΔG_f°, for glucose, $C_6H_{12}O_{6(s)}$ at 298 K. Specify units.

(D) At 298 K, glucose burns in oxygen to form only $CO_{2(g)}$ and $H_2O_{(\ell)}$. Calculate the expected value of the standard enthalpy of combustion, $\Delta H_{\text{comb}}^\circ$, for glucose, $C_6H_{12}O_{6(s)}$. Specify units.

CHAPTER 9

ACID-BASE SYSTEMS

Acids and bases are key players in the Advanced Placement Chemistry game. You should be able to use acid-base concepts to write net ionic equations, to form complex ions, and to solve stoichiometry, equilibrium, and thermodynamics problems.

ACIDS AND BASES – SOME DEFINITIONS

The designation of certain reactions as acid-base reactions is intended to help you organize information about reactions that illustrate similar properties. Three categories of acid-base reactions are included in the AP course:

- Arrhenius
- Bronsted/Lowry
- Lewis

For each category, a definition of acid and base is established and a characteristic reaction is described. See Figure 9.1.

Figure 9.1 Comparing acid-base systems

		Arrhenius	**Bronsted/Lowry**	**Lewis**
DEFINITIONS	**An acid is a substance...**	whose only positive ion in water solution is H^+ ion	which acts as a proton (H^+) donor	which accepts a share in a pair of electrons
	examples	HCl, HNO_3	H_3O^+, HSO_4^-	BF_3, Fe^{3+}
	A base is a substance...	whose only negative ion in water solution is OH^- ion	which acts as a proton (H^+) acceptor	which donates a share in a pair of electrons
	examples	$NaOH$, KOH	NH_3, SO_4^{2-}	CN^-, $C_2O_4^{2-}$
	Characteristic reaction	acid + base → salt + water	$\text{acid}_1 + \text{base}_1 \rightarrow \text{acid}_2 + \text{base}_2$ acid_1 and base_2 are called "a conjugate pair"	covalent bond forms between acid and base
	examples	$HCl + NaOH \rightarrow NaCl + H_2O$ neutralization	$HSO_4^- + NH_3 \rightarrow NH_4^+ + SO_4^{2-}$ proton transfer	$Fe^{3+} + 6CN^- \rightarrow Fe(CN)_6^{3-}$ complexation

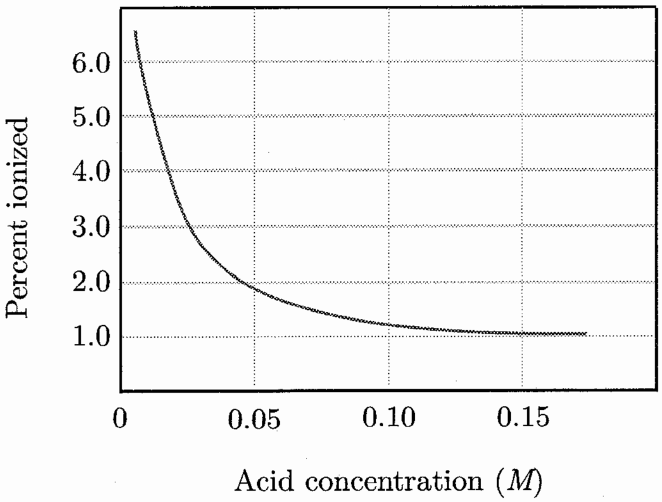
Strong and Weak Acids and Bases

In Arrhenius acid-base systems, the terms strong and weak refer to the extent of ion formation. Strong acids are nearly 100% ionized; weak acids can often be much less than 1% ionized. The graph in Figure 9.2 below shows how percent ionization decreases as concentration increases.

Similarly, strong bases are 100% dissociated with weak bases undergoing much less dissociation.

Common strong acids: H_2SO_4, HCl, HNO_3, HBr, HI, $HClO_4$

Figure 9.2 Percent ionization of a weak acid



Common strong bases: KOH, NaOH and other hydroxides of Group 1 metals,
$Sr(OH)_2$, $Ba(OH)_2$

In Bronsted-Lowry systems, strong acids donate protons readily because the bond between hydrogen and the remainder of the molecule or ion is relatively weak. Strong bases form strong bonds between the donated proton and its new destination. Tables of Bronsted-Lowry acids and their conjugate bases as shown in Figure 9.3 are often presented in order of decreasing acid strength. Note that the conjugate of any acid is the corresponding base which you can determine by removing one H^+ from the acid form. It is often useful to think of a Bronsted-Lowry acid-base reaction as simply competition between two bases for a proton: the stronger base wins.

Figure 9.3

RELATIVE STRENGTHS OF ACIDS IN AQUEOUS SOLUTION AT 1 atm AND 298 K

	Conjugate Pairs *ACID* *BASE*	
stronger acid	$HI = H^+ + I^-$	weaker base
	$HBr = H^+ + Br^-$	
	$HCl = H^+ + Cl^-$	
	$HNO_3 = H^+ + NO_3^-$	
	$H_2SO_4 = H^+ + HSO_4^-$	
	$H_2O + SO_2 = H^+ + HSO_3^-$	
	$HSO_4^- = H^+ + SO_4^{2-}$	
	$H_3PO_4 = H^+ + H_2PO_4^-$	
	$Fe(H_2O)_6^{3+} = H^+ + Fe(H_2O)_5(OH)^{2+}$	
	$HNO_2 = H^+ + NO_2^-$	
	$HF = H^+ + F^-$	
	$Cr(H_2O)_6^{3+} = H^+ + Cr(H_2O)_5(OH)^{2+}$	
	$CH_3COOH = H^+ + CH_3COO^-$	
	$Al(H_2O)_6^{3+} = H^+ + Al(H_2O)_5(OH)^{2+}$	
	$H_2O + CO_2 = H^+ + HCO_3^-$	
	$HSO_3^- = H^+ + SO_3^{2-}$	
	$H_2S = H^+ + HS^-$	
	$H_2PO_4^- = H^+ + HPO_4^{2-}$	
	$NH_4^+ = H^+ + NH_3$	
	$HCO_3^- = H^+ + CO_3^{2-}$	
	$HPO_4^{2-} = H^+ + PO_4^{3-}$	
	$HS^- = H^+ + S^{2-}$	
	$H_2O = H^+ + OH^-$	
	$OH^- = H^+ + O^{2-}$	
weaker acid	$NH_3 = H^+ + NH_2^-$	stronger base

Neutralization

When an Arrhenius acid is mixed with an Arrhenius base, neutralization occurs. The quantitative principle involved specifies that one mole of mole H^+ exactly neutralizes one mole of OH^-. To manage the quantitative relationships in a neutralization reaction, there are generally four facts to be obtained: three are usually observations from the laboratory procedure under consideration; the fourth fact is calculated using these observations. For example, if the results of an experiment shows that 36.5 mL of 0.152 M $KOH_{(aq)}$ is neutralized by 27.3 mL of $HNO_{3(aq)}$, the apparent concentration of the HNO_3 solution can be calculated.

$$\frac{0.0365 \text{ L } KOH_{(aq)}}{0.0273 \text{ L } HNO_{3(aq)}} \times \frac{0.152 \text{ mol } KOH}{1.00 \text{ L } KOH_{(aq)}} = \frac{0.203 \text{ mol } HNO_3}{1.00 \text{ L } HNO_{3(aq)}}$$

Titration

When titration procedures are used to determine unknown concentration of an acid or base, there are two common methods of determining the point of exact neutralization.

Indicators In one kind of experiment, an indicator is used to indicate the endpoint of a titration, that is the conditions at which the exact neutralization has occurred and excess H^+ or OH^- ions become present in the solution. The choice of indicator is determined by the pH of the end product solution. Figure 9.4 shows the type of indicator needed, based on the properties of the acid/base reactants. Figure 9.5 is a list of frequently used indicators and the pH range over which their color changes are observed.

Figure 9.4 Titration: choosing an indicator

Neutralization of	Choose an indicator that changes color when the mixture of reactants is
Strong acid + strong base	neutral; pH approximately 7
Strong acid + weak base	is acidic; pH less than 7
Weak acid + strong base	is basic; pH greater than than 7

Figure 9.5 Common Acid-Base Indicators

Indicator	Approximate pH Range for Color Change	Color Change
methyl orange	3.2–4.4	red to yellow
bromcresol green	3.8–5.4	yellow to blue
litmus	5.5–8.2	red to blue
bromthymol blue	6.0–7.6	yellow to blue
thymol blue	8.0–9.6	yellow to blue
phenolphthalein	8.2–10	colorless to pink

pH Titrations In another kind of experiment, the pH of a reaction mixture is monitored as one reactant is added in small quantities – perhaps even drop-wise – to a solution of the other reactant. The observed values of pH are plotted as a dependent variable with volume of titrant added as the independent variable. Refer to your textbook for graphs of various pH titrations.

Hydrolysis of salts

Some salts dissolve in water to form solutions that are distinctly acidic or basic. Such salts are said to "hydrolyze". The conjugate bases of weak acids, often anions such as CH_3COO^- or $CO_3{}^{2-}$, react with water to form basic solutions.

$$\text{anion hydrolysis: } CO_3{}^{2-} + H_2O \rightleftharpoons HCO_3{}^- + OH^-$$

Some hydrated cations of transition elements such as Fe^{3+} react with water to form acidic solutions.

$$\text{cation hydrolysis: } Fe(H_2O)_6{}^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5OH^{2+} + H_3O^+$$

Buffer solutions

A buffer solution is a solution of a weak acid and its conjugate base, at concentrations such that the pH of the solution does not change appreciably even though a substantial amount of H^+ or OH^- is added to the solution. The weak acid acts as a proton donor, neutralizing any added OH^-; the conjugate base accepts H^+, neutralizing any added acid.

Note that the capacity of a buffer is exceeded when the amount of proton donor added is greater than the amount of proton acceptor available in the buffer and vice versa.

Amphiprotic (amphoteric) compounds

In the Arrhenius system, an amphiprotic substance acts as an acid in the presence of a strong base and acts as a base in the presence of a strong acid. Aluminum hydroxide, $Al(OH)_3$, is a common example:

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

In the Bronsted Lowry system, an amphiprotic substance contains a proton that can be donated as well as an unshared electron pair that is available to accept a proton. The hydrogen carbonate ion, $HCO_3{}^-$, is a common example:

$$\text{as a proton donor: } HCO_3{}^- + OH^- \rightarrow H_2O + CO_3{}^{2-}$$

$$\text{as a proton acceptor: } HCO_3{}^- + H_3O^+ \rightarrow H_2O + H_2O + CO_2$$

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

III. Reactions

A. Reaction Types

1. Acid-base reactions; concepts of Arrhenius, Bronsted-Lowry, and Lewis; coordination complexes; amphoterism
2. Precipitation reactions

C. Equilibrium

2 Quantitative treatment

b. Equilibrium constants for reactions in solution

(1) Constants for acids and bases; pK; pH

(3) Common ion effect; buffers; hydrolysis

from the list of CHEMICAL CALCULATIONS

5. ... titration calculations

from the list of EQUATIONS & CONSTANTS

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$K_b = \frac{[\mathrm{OH^-}][\mathrm{HB^+}]}{[\mathrm{B}]}$$

$$\begin{aligned} K_w &= [\mathrm{OH^+}][\mathrm{H^+}] = 10^{-14} \text{ @ } 25^\circ\mathrm{C} \\ &= K_a \times K_b \end{aligned}$$

$$\mathrm{pH} = -\log[\mathrm{H^+}],\ \mathrm{pOH} = -\log[\mathrm{OH^-}]$$

$$14 = \mathrm{pH} + \mathrm{pOH}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{pOH} = \mathrm{p}K_b + \log\frac{[\mathrm{HB^+}]}{[\mathrm{B}]}$$

$$\mathrm{p}K_a = -\log K_a,\ \mathrm{p}K_b = -\log K_b$$

from the list of RECOMMENDED EXPERIMENTS

6. Standardization of a solution using a primary standard
7. Determination of concentration by acid-base titration, including a weak acid or weak base
11. Determination of appropriate indicators for various acid-base titrations; pH determination
13. Determination of enthalpy change associated with a reaction
15. Synthesis of a coordination compound and its chemical analysis
19. Preparation and properties of buffer solutions

Multiple Choice Questions

Questions 1–5: The set of lettered choices below is a list of chemical compounds that are soluble in water and take part in acid-base reactions. Select the one lettered choice that best fits each numbered statement. A choice may be used once, more than once, or not at all.

(A) BF_3
(B) C_2H_5OH
(C) CH_3COOH
(D) $FeCl_3$
(E) $KHSO_3$

1. acts as a Lewis acid but not a Bronsted-Lowry acid

2. illustrates amphiprotic behavior in aqueous solution

3. dissolves as a weak electrolyte

4. undergoes hydrolysis in water to produce a solution that is acidic

5. reacts with an alcohol to form an ester

---

6. Which is the best description of the behavior of a Lewis base in a chemical reaction?

(A) electrophilic
(B) heterophilic
(C) homophilic
(D) hydrophilic
(E) nucleophilic

7. Which equation best illustrates the ionization of liquid ammonia?

(A) $NH_3 \rightleftharpoons 3H^+ + N^{3-}$
(B) $NH_3 \rightleftharpoons NH_2{}^- + H^+$
(C) $NH_3 + NH_3 \rightleftharpoons NH_4{}^+ + NH_2^-$
(D) $H_2O + NH_3 \rightleftharpoons H_3O^+ + NH_2^-$
(E) $H_2O + NH_3 \rightleftharpoons NH_4{}^+ + OH^-$

8. Which substance is a polyprotic acid in water solution?

I. CH_3COOH
II. C_2H_5OH
III. $H_2C_2O_4$

(A) I only
(B) III only
(C) II and III only
(D) I and II only
(E) I, II, and III

9. Consider the three acids: HF, HSO_4^- and $H_2PO_4^-$.

Which list includes only conjugate bases of the acids given above?

(A) OH^-, HPO_4^{3-}
(B) F^-, SO_4^{2-} and HPO_4^{2-}
(C) OH^-, SO_4^{2-} and PO_4^{3-}
(D) OH^-, SO_4^{2-} and HPO_4^{2-}
(E) H_2F^+, H_2SO_4 and H_3PO_4

10. Which identifies the products that form when N_2O_5 dissolves in water?

(A) H^+ and NO_3^-
(B) NO_2 and H_2O_2
(C) H_2, O_2 and N_2
(D) NH_4^+, OH^- and O_2
(E) NH_4^+, NH_2^- and O_2

11. Which pair of equations illustrates the amphiprotic behavior of $H_2PO_4^-$?

I. $H_2PO_4^- + OH^- \rightarrow H_2O + HPO_4^{2-}$
II. $H_2PO_4^- + 2OH^- \rightarrow 2H_2O + PO_4^{3-}$
III. $H_2PO_4^- + H_3O^+ \rightarrow H_2O + H_3PO_4$
IV. $H_2PO_4^- + CH_3COOH \rightarrow CH_3COO^- + H_3PO_4$
V. $H_2PO_4^- + 2NH_2^- \rightarrow 2NH_3 + PO_4^{3-}$

(A) I and II only
(B) III and IV only
(C) II and V only
(D) I and V only
(E) IV and V only

12. Which occurs when potassium amide, KNH_2, dissolves in water?

(A) K^+ is hydrolyzed to KH.
(B) Nitrogen is oxidized from −3 to 0.
(C) Nitrogen is reduced from +1 to 0.
(D) A proton is transferred to NH_2^-.
(E) A proton is transferred from NH_2^-.

13. Which oxide is a basic anhydride?

I. Na_2O
II. BaO
III. ZnO

(A) I only
(B) III only
(C) II and III only
(D) I and II only
(E) I, II, and III

14. Which range includes the pH that results when 0.10 mole $NaOH_{(s)}$ is added to 100. mL of 1.0 *M* HCl solution?

(A) between 1 and 4
(B) between 4 and 6.5
(C) between 6.5 and 7.5
(D) between 7.5 and 10
(E) between 10 and 14

15. Each list contains at least one species that could illustrate amphiprotic behavior EXCEPT

(A) HNO_3, HCl, HS^-
(B) CO_3^{2-}, Br^-, NH_4^+
(C) HCO_3^-, HSO_4^-, NH_3
(D) $H_2PO_4^-$, NH_2^-, ClO_3^-
(E) H_3PO_4, $Al(OH)_3$, $Zn(OH)_2$

16. All of the following apply to a solution prepared by adding potassium carbonate to water EXCEPT

(A) The pH increases to a value greater than 7.
(B) The aqueous phase of the system remains colorless.
(C) The electric conductivity of the solution increases.
(D) The concentration of OH^- ions in solution increases.
(E) The dissolved species are molecules of potassium carbonate.

17. Which occurs when water is added to a solution of HCl?

	pH	**$[H_3O^+]$**
(A)	increases	decreases
(B)	increases	remains the same
(C)	decreases	increases
(D)	decreases	increases
(E)	remains the same	decreases

18. For CH_3COOH, $K_a = 1.8 \times 10^{-5}$

Which could be added to 1.0 liter of 0.10 M CH_3COOH to form a buffer solution with pH between 4 and 5?

I. 0.050 mol HCl
II. 0.050 mol NaOH
III. 0.050 mol $NaCH_3COO$

(A) I only
(B) II only
(C) I and II only
(D) II and III
(E) I and III only

Questions 19-23: A sample containing precisely 25.0 mL of a solution of H_2SO_4 of unknown concentration is analyzed using a solution of NaOH of known concentration. The NaOH is titrated slowly into the H_2SO_4 solution from a buret. When neutralization occurs as shown by change in color of the indicator, the final value for the volume of $NaOH_{(aq)}$ is recorded.

NaOH solution	0.125 M
Starting volume, $NaOH_{(aq)}$	1.4 mL
Final volume, $NaOH_{(aq)}$	27.8 mL

19. Which identifies the spectator ions in this reaction?

(A) The only spectator ion is Na^+.
(B) The only spectator ion is SO_4^{2-}.
(C) Both Na^+ and SO_4^{2-} are spectator ions.
(D) Both Na^+ and HSO_4^- are spectator ions.
(E) There are no spectator ions in this reaction.

20. As this reaction proceeds, the concentration of Na^+ in the reaction mixture

(A) increases and the concentration of SO_4^{2-} increases
(B) increases and the concentration of SO_4^{2-} decreases
(C) remains the same and the concentration of SO_4^{2-} remains the same
(D) remains the same and the concentration of SO_4^{2-} increases
(E) remains the same and the concentration of SO_4^{2-} decreases

21. Which expression gives the molarity of the H_2SO_4 solution?

(A) $\dfrac{0.0264 \times 0.125 \times 2}{0.0250}$

(B) $\dfrac{0.0250 \times 2}{0.0264 \times 0.125}$

(C) $\dfrac{0.0264 \times 0.125}{0.0250 \times 2}$

(D) $\dfrac{0.0250 \times 0.125}{0.0264 \times 2}$

(E) $\dfrac{0.0250 \times 0.125 \times 2}{0.0264}$

22. If, unknown to the technician, some water had been added to the unknown H_2SO_4 solution by mistake after its precise volume had been measured, which value in the table of observations, if any, would be changed? If there were a change, in which direction would the change occur?

(A) The final volume of $NaOH_{(aq)}$ would be reported larger.

(B) The final volume of $NaOH_{(aq)}$ would be reported smaller.

(C) The molarity of the NaOH solution would be reported larger.

(D) The molarity of the NaOH solution would be reported smaller.

(E) No change would be reported in any of the three values.

23. If, unknown to the technician, some water had been added to the NaOH solution of known concentration by mistake before the final volume had been measured, which value in the table of observations, if any, would be changed? If there were a change, in which direction would the change occur?

(A) The final volume of $NaOH_{(aq)}$ would be reported larger.

(B) The final volume of $NaOH_{(aq)}$ would be reported smaller.

(C) The molarity of the NaOH solution would be reported larger.

(D) The molarity of the NaOH solution would be reported smaller.

(E) No change would be reported in any of the three values.

24. Which gives the mass action expression for hydrolysis of the $CO_3{}^{2-}$ ion?

(A) $\dfrac{[H^+][OH^-]}{[CO_3{}^{2-}]}$

(B) $\dfrac{[CO_3{}^{2-}]^2}{[H^+][OH^-]}$

(C) $\dfrac{[HCO_3{}^-][H^+]}{[CO_3{}^{2-}]}$

(D) $\dfrac{[CO_3{}^-][H^+]}{[HCO_3{}^-]}$

(E) $\dfrac{[HCO_3{}^-][OH^-]}{[CO_3{}^{2-}]}$

25. When a sample of 0.0060 M NaOH is diluted with an equal amount of water, the pH of the resulting solution is closest to

(A) 10.2
(B) 10.8
(C) 11.0
(D) 11.5
(E) 12.5

Free-Response Questions

26. A sample of 0.200 M solution of KHC_2O_4 (molar mass: 128 g) is used to determine the concentration of an unknown solution of KOH. Phenolphthalein is used as the indicator.

    (A) What mass of KHC_2O_4 is required to prepare 750. mL of 0.200 M KHC_2O_4 solution?

    (B) In one experiment, 25.0 mL of the unknown KOH solution is placed in a beaker. Added to the KOH solution in the beaker is 25.0 mL of water and a few drops of phenolphthalein. The KHC_2O_4 solution is titrated into the dilute base.

    (1) The volume of KHC_2O_4 solution required to reach equivalence is 26.7 mL. What is the concentration of the original KOH solution?

    (2) What specific observation identifies the endpoint of the titration?

    (3) What is the molar concentration of $K^+{}_{(aq)}$ in the reaction mixture at the equivalence point?

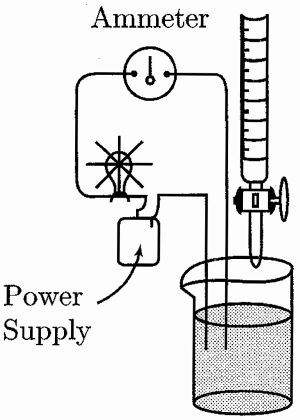
    (C) In a second experiment, 25.0 mL of the same unknown KOH solution as used in part (B) and 25.0 mL of water are placed in the beaker, as above. An additional 50.0 mL of water is added to the KOH solution in the beaker. Again the KHC_2O_4 solution of known concentration is titrated into the dilute base.

    (1) Compared to the first experiment in (B) above, is the volume of $KHC_2O_{4(aq)}$ needed to reach the equivalence point of this second experiment greater, smaller or the same? Explain.

    (2) Compared to the first experiment in (B) above, is the molar concentration of $K^+{}_{(aq)}$ in the reaction mixture at the equivalence point of this second experiment greater, smaller or the same? Explain.

    (D) In another experiment, the technician, in error, used potassium acid oxalate hydrate, $KHC_2O_4 \cdot H_2O$ (molar mass: 146 g) without adjusting for different molar mass as if it were the assigned anhydrous compound for the preparation of the solution in Part (A). What effect would this have on the value subsequently reported for the molarity of the KOH solution compared to the true value for that molarity? Explain.

27. In the experiment described below, $Ba(OH)_{2(aq)}$ of unknown concentration is titrated against a precisely measured 25.0 mL volume of 0.0500 M $H_2SO_{4(aq)}$. Phenolphthalein, added to the acid solution, is used as an indicator. A system to measure conductivity is set up with a lamp connected in series with an ammeter and the solution to be tested. Assume constant temperature is maintained.



Volume $H_2SO_{4(aq)}$ used: 25.0 mL

Volume $Ba(OH)_{2(aq)}$ added	**Observations**
26.7 mL	lamp goes out
27.8 mL	lowest current reading
28.3 mL	solution turns pink
28.6 mL	lamp goes on

(A) Write the net ionic equation for this reaction.

(B) Explain why the light goes out but the ammeter reading never drops to zero.

(C) Explain why the light goes back on when the volume of $Ba(OH)_{2(aq)}$ added is 28.6 mL.

(D) Calculate the concentration of the barium hydroxide solution using the minimum value of conductance as the best indicator of the endpoint.

(E) A lower value for the concentration of the barium hydroxide would result if the color change of the indicator, instead of the minimum conductance reading, were used to indicate the endpoint. Explain.

28. In each of two flasks, a solution is prepared by placing 0.25 mol acetic acid, CH_3COOH, and 0.25 mol acetate ions, CH_3COO^-, in sufficient water to prepare 1.00 liter of solution. These two solutions are used for the experiments described in parts (C) and (D) below.

(A) What is a buffer solution? What characteristics make this solution a buffer solution?

(B) Draw the Lewis structures for the acetic acid molecule and the hydronium ion.

(C) Added to the solution in one flask is 0.15 mol $KHSO_{4(s)}$. What is the effect on $[CH_3COOH]$ and $[CH_3COO^-]$? Account for your answer in terms of numbers of moles of protons transferred. Has the capacity of the buffer been exceeded? Explain.

(D) Added to the solution in the second flask is 0.40 mol $NaOH_{(s)}$. What is the effect on $[CH_3COOH]$ and $[CH_3COO^-]$? Account for your answer in terms of numbers of moles of protons transferred. Has the capacity of the buffer been exceeded? Explain.

29. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. In all cases a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

(A) Excess 3 *M* ammonia is added to a solution of copper(II) sulfate.

(B) Excess sodium hydroxide solution is added to a suspension of aluminum hydroxide.

(C) Equal volumes of 0.10 *M* sodium hydrogen phosphate and 0.10 *M* hydrochloric acid are mixed.

(D) A lump of zinc metal is added to excess 1.0 *M* hydrochloric acid.

(E) Solid potassium oxide is added to water.

(F) Solid iron(II) sulfide is added to 6 *M* sulfuric acid.

(G) Solid ammonium carbonate is added to a warmed solution of sodium hydroxide.

(H) Sulfur dioxide gas is bubbled into water.

5

CHAPTER 10

ELECTROCHEMISTRY

Electrochemistry appears on the Advanced Placement Chemistry examination as net ionic equations, in galvanic and electrolytic cell problems, and in equilibrium and thermodynamics problems. You should be ready to address electrochemistry topics as part of many questions on the AP Chemistry exam.

Electrochemistry, that is, oxidation and reduction, deals with electrons moving in a path from the species oxidized to the species reduced. There are a number of mnemonic devices to help you remember this fundamental principle. One is OIL RIG, or Oxidation Is Loss while Reduction Is Gain of electrons.

OXIDATION NUMBERS

You will need to assign oxidation numbers to atoms in compounds or polyatomic ions as part of multiple choice questions as well as free response questions.

Rules for Oxidation Numbers

To facilitate the bookkeeping of electron transfers, oxidation numbers are assigned to each atom represented in each molecule or ion. The oxidation number should not be treated as the actual charge on an atom in the molecule or ion. Rules for assigning oxidation numbers (ON) can be summarized as follows:

1. Atoms in uncombined elemental form have zero as an oxidation number. Thus atoms in Fe, F_2, P_4 or S_8 all have ON of 0.
2. Monatomic ions have an oxidation number equal to the charge on the ion. Hence the ON of chloride is -1 while that of sulfide is -2.
3. When combined with other atoms, atoms of group 1 (alkali metals) always have ON of $+1$; atoms of group 2 (alkaline earth metals) always have ON of $+2$.
4. Combined oxygen always has ON of -2 (except for peroxides such as H_2O_2 where ON for oxygen is -1 or when combined with fluorine as OF_2 where ON for oxygen is $+2$).
5. Combined hydrogen always has ON of $+1$ (except for hydrides such as CaH_2 where ON for H is -1).
6. Combined fluorine always has ON of -1.
7. The ON of any other atom must be determined from its context. The sum of all ON within a compound must be zero (thus the ON of sulfur in H_2SO_4 must be $+6$). Within a polyatomic ion, the sum of ON must equal the overall charge on the ion. (Thus, the ON of phosphorus in $PO_4{}^{3-}$ must be $+5$.)

Oxidation = increase in ON, explained as loss of electrons

Reduction = decrease in ON, explained as gain of electrons

Balancing Redox Equations

There are various methods used to help with balancing redox equations. Here is one that never fails. It is sometimes called the "ion/water" or "ion/electron" method.

1. Starting with the given system or unbalanced equation, separate the reaction into two half-reactions. One must contain an oxidation while the other must include a reduction.
2. Balance each half-reaction separately.
   a. Balance the element oxidized or reduced.
   b. Balance any elements other than oxygen or hydrogen.
   c. Balance oxygen by adding water in the form of H_2O.
   d. In acidic solution, balance hydrogen by adding protons (H^+). In basic solution, balance hydrogen by adding water in the form H-OH, then immediately add the same number of hydroxides (OH^-) to the opposite side of the equation.
   e. Balance the total charge on each side of each half-reaction by adding electrons (e^-) to the side that is more positive.
3. Choose a multiplier for each half-reaction such that the number of electrons lost is equal to the number of electrons gained in the separate half-reactions. You will remember this technique from math class as being similar to determining the LCM (least common multiple). For example, if the oxidation loses 2 electrons while the reduction gains 3 electrons, the least common multiple is 6. Thus you should multiply the oxidation by 3 and the reduction by 2.
4. Add the two half-reactions together. The electrons should cancel out from each side of the equation. You may be able to cancel other species as well. Water as well as hydroxide and hydrogen ions will frequently cancel. Remember that H_2O and H–OH both mean water; they are written differently here to help balance oxygen and hydrogen efficiently.
5. Check to be sure that there is the same total charge on each side (It may be zero but is not required to be zero, just the same). Then check the total number of oxygen atoms on each side. If both the total charge and the number of oxygens balance, it is highly likely that you have balanced the overall reaction correctly.

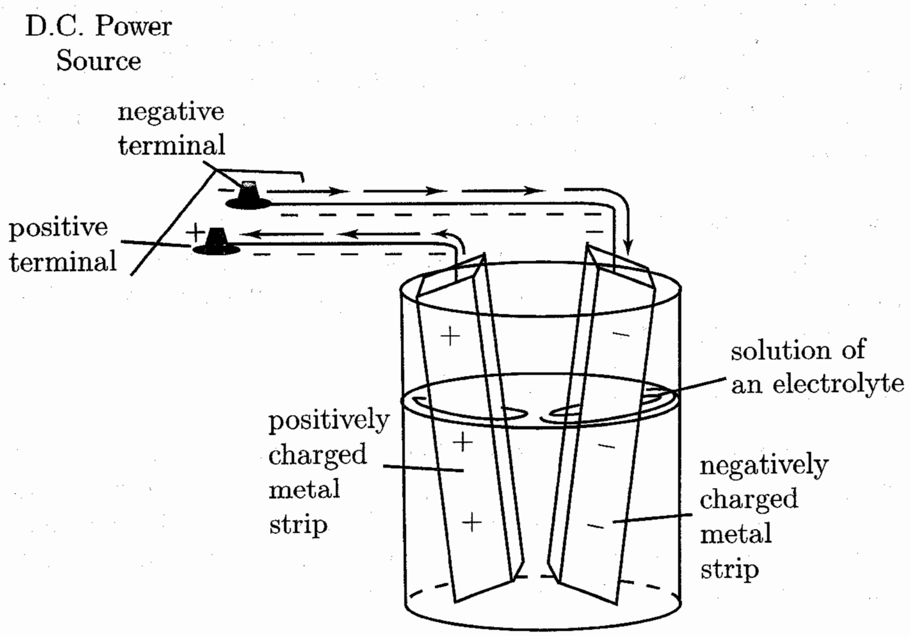
   There are illustrations of balancing redox equations in the problems that follow this chapter.

Electrolytic and Galvanic Cells

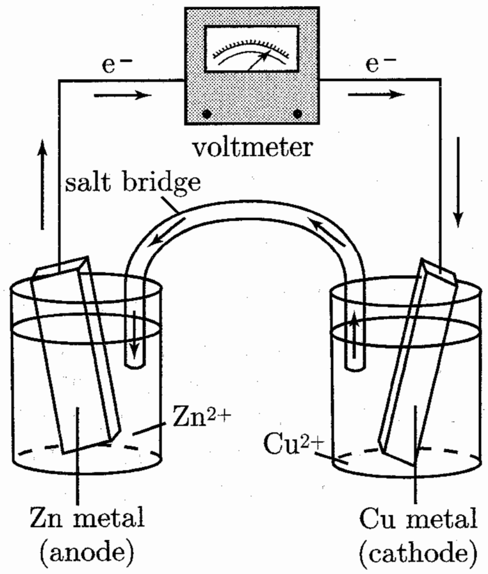
In a galvanic (or voltaic) cell, chemical differences cause an electric difference to occur. Potential differences between substances cause electrons to flow as long as half-cells are separated by a salt bridge and external circuit. If the half-cells operate in physical contact with each other, the potential difference is presented as heat rather than as flow of electrons. No flow of electrons would be available to use in an external circuit.

An electrolytic cell represents the opposite situation: an electric current causes chemical changes to occur. An externally-supplied electric current forces chemical change to occur. In either electrolytic or galvanic cells, oxidation occurs at the anode and reduction at the cathode. Electrons flow through the external circuit from the anode to the cathode. Figure 10.1 provides a useful comparison of these two kinds of cells.

Figure 10.1 Comparing electrolytic and galvanic cells



Electrolytic cell



Galvanic cell

Using a table of standard reduction potentials

Since the oxidation and reduction half-reactions are combined to form an overall reaction to describe the electrochemical cell, so too are the values for the half-cells from the Standard Reduction Potential (SRP) table. To calculate E°, the standard voltage for a cell, you must combine the separate values for the two half-reactions. The SRP value for the reaction identified as oxidation (see #3 above) changes sign since the reduction equation from the table is reversed to become an oxidation. Thus $Zn^{2+} \rightarrow Zn$ shows a SRP of (−0.76 V); when expressed as an oxidation, $Zn \rightarrow Zn^{2+}$, the value for the half-reaction becomes (+0.76 V). The overall voltage for the cell described is determined by adding together the values for an oxidation and a reduction to give a total positive value. When the zinc oxidation half-reaction is combined with the reduction of copper(II) to copper, a total voltage of +1.10 V is created.

$$E^\circ = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}} = -(-0.76\text{ V}) + (0.34\text{ V}) = +1.10\text{ V}$$

When a reaction or half-reaction is multiplied by any integer to balance an overall reaction, its standard reduction potential remains unchanged. (Three Cl_2 molecules pull six electrons with the same force that one Cl_2 pulls two electrons.)

Nonstandard conditions - The Nernst equation

The "nought" ("°") indicates standard conditions of pressure (one atmosphere), temperature (298 K), and concentration (1 *M*) of all solutions. If any of these conditions differs from the standard, then the voltage in the cell will differ. To calculate this different voltage, we can use the Nernst equation. In its full form, any difference in pressure, temperature, or concentration can be accommodated:

$$E = E^\circ - \left(\frac{RT}{n\Im}\right) \ln Q$$

where E° = the cell electromotive force (emf) as calculated from a table of standard reduction potentials (SRP)

$R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$

T = temperature in kelvins

n = number of moles of electrons transferred in the redox

$\Im$ = Faraday's constant, $96{,}485\text{ mol}^{-1}\text{ V}^{-1}$ (coulombs mol^{-1})

Q = trial reaction quotient, including actual concentrations of all species.

However, because ion concentrations in solution are unaffected by the pressure over the surface of the solution and the standard temperature (298 K) is frequently assumed, a form of the Nernst equation is widely used to allow calculation with only differences in concentration. The constants of temperature, concentration, and faraday, in effect, combine to form a new constant. "Nernst lite" also uses base-10 log rather than the natural log.

$$E = E^\circ - \left(\frac{0.0592}{n}\right) \log Q$$

VOCABULARY: OXIDATION/REDUCTION

Redox	a reaction process; oxidation accompanied by reduction
Oxidation	increase in oxidation number, explained as loss of electrons
Reduction	decrease in oxidation number, explained as gain of electrons
Reducing Agent	reactant species that loses electrons and gets oxidized; causes reduction of another species
Oxidizing Agent	reactant species that gains electrons and gets reduced; causes oxidation of another species
Oxidation Number	assigned to each atom in a chemical species to indicate apparent charge
Half-Reaction	a balanced equation that describes either oxidation or reduction; describes one half of the overall redox process

Electrochemical cells and their components

Electrochemical cell	a device in which the energy from a redox reaction is used to produce the flow of electrons; uses two separated redox half-reactions to generate electrical current through an external circuit; synonyms are voltaic, galvanic or simply chemical cell
Electrodes	surfaces of metal plates, grids, or wires, where electrons are gained and lost by metal atoms and ions; can also refer to the entire assembly of apparatus associated with the metal electrode
Anode	the electrode where oxidation occurs
Cathode	the electrode where reduction occurs
Cell potential	difference in electrical potential between the two electrodes of the two half cells, measured in volts
Reduction potential	conventional tabulated E° values for half-reactions compared to the standard hydrogen electrode defined as $E^\circ = 0.00$ V
Salt Bridge	a physical pathway that "completes the circuit" in some electrochemical cells; allows ions to migrate through a tube containing a solution of generally unreactive ions; this purpose can also be served by a porous barrier between half cells

Electrolytic cells and their components

Electrolytic Cell	a device that uses electrical energy to produce a chemical change that would otherwise not occur spontaneously
Electrolysis	the process of using electrical current to drive redox reactions
Electroplating	a process in which electrolysis used to deposit one metal on the surface of another metal or other substance.
Electrodes	are named anode and cathode using same definitions as with electrochemical cells, above

REDOX: REDUX – a brief summary

1. Oxidation and reduction always occur together since electrons must move from one species to another.
2. The number of electrons lost in oxidation must equal the number of electrons gained in reduction.
3. When comparing half-reactions to determine direction of electron flow, the half-reaction with the more negative reduction potential occurs at the anode of a galvanic cell as oxidation. (This species hold electrons more loosely.)
4. The half-reaction with the more positive reduction potential occurs at the cathode of a galvanic cell as reduction. (This species attracts electrons more strongly.)
5. When a reaction or half-reaction is multiplied by any integer to balance an overall reaction, its reduction potential remains unchanged. (Three Cl_2 molecules pull six electrons with the same force that one Cl_2 pulls two electrons.)
6. Commonly used line notation for a galvanic cell:

   anode/anode solution // cathode solution/cathode
   (where // represents a salt bridge or porous barrier)

   For example, in the Daniell cell, $Zn/Zn^{2+}//Cu^{2+}/Cu$ means

$$\begin{array}{rr} Zn \rightarrow Zn^{2+} + 2e^- & -(-0.76)\ V \\ Cu^{2+} + 2e^- \rightarrow Cu & 0.34\ V \\ \hline Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu & E^\circ_{cell} = 1.10\ V \end{array}$$

7. A spontaneous reaction is signified by a positive cell voltage, a negative Gibbs Free Energy change, and an equilibrium constant with a positive exponent (constant > 1). To link these:

$$\Delta G^\circ = -n\Im E^\circ = -RT\ln K_{eq}$$

8. During electrolysis, the number of moles of electrons transferred depends on the current (amperage rate of flow) and the time during which the current flows. To link these ideas, remember that an ampere is defined as a coulomb per second:

$$A = \frac{C}{s} \qquad \text{Ampere} = \frac{\text{coulomb}}{\text{sec}}$$

   The link between charge and moles of electrons (and indirectly the number of moles of reactants or products) is given by the definition of the faraday as 96,485 coulombs per mole of electrons:

$$\Im = \frac{96{,}485\ C}{\text{mol } e^-}$$

   Thus, multiplying amperage by time by inverted faraday will reveal the number of moles of electrons released for an electrolytic reaction.

$$\text{Mol } e^- \text{ produced} = \text{amperage} \times \text{time} \times \Im^{-1}$$

$$= \left(\frac{C}{sec}\right) \times (sec) \times \left(\frac{1\ \text{mol } e^-}{96{,}485\ C}\right)$$

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

III. Reactions

A. Reaction types

3. Oxidation-reduction reactions
   - a. Oxidation number
   - b. The role of the electron in oxidation-reduction
   - c. Electrochemistry: electrolytic and galvanic cells; Faraday's laws; standard half-cell potentials; Nernst equation; prediction of the direction of redox reactions

from the list of CHEMICAL CALCULATIONS

7. Faraday's laws of electrolysis (stoichiometry using moles of electrons)
9. Standard electrode potentials and their use; Nernst equation

from the list of EQUATIONS & CONSTANTS

$I = \frac{q}{t}$ where I = current (amperes),

q = charge (coulombs) and t = time (seconds)

$$\Delta G^\circ = -n\Im E^\circ = -RT\ \ln K_{eq}$$

$$\Delta G = \Delta G^\circ + RT\ \ln Q = \Delta G^\circ + 2.303RT\ \log Q$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{n\Im}\ln Q = E^\circ_{cell} - \frac{0.0592}{n}\log Q \text{ @ } 25^\circ C$$

from the list of RECOMMENDED EXPERIMENTS

From the laboratory list:

8. Determination of concentration by oxidation-reduction titration
9. Determination of mass and mole relationship in a chemical reaction
20. Determination of electrochemical series
21. Measurements using electrochemical cells and electroplating

Multiple Choice Questions

Questions 1-5: The set of lettered choices is a list of ions that participate in oxidation reduction reactions. Select the one lettered choice that best fits each numbered description. A choice may be used once, more than once or not at all.

(A) CO_3^{2-}
(B) CrO_4^{2-}
(C) MnO_4^-
(D) NO_3^-
(E) Fe^{2+}

1. includes the species with a +7 oxidation number
2. includes the species with a +6 oxidation number
3. reacts with a reducing agent in acid solution such that the oxidation number of the metal becomes +2
4. when oxidized, forms a cation with a +3 oxidation number
5. reacts with a reducing agent in acid solution to form a brown gas

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Questions 6-9:

$$Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag \qquad E^\circ = 3.17\ V$$

The above equation refers to a common electrochemical cell.

6. Which expression gives the value of ΔG° in kJ mol^{-1} for this reaction?

   (A) $-2 \times 8.31 \times 3.17 \times 1000$

   (B) $\dfrac{(-2 \times 96{,}500 \times 3.17)}{8.31}$

   (C) $\dfrac{(-2 \times 96{,}500 \times 3.17)}{1000}$

   (D) $\dfrac{(-2 \times 96{,}500)}{(3.17 \times 8.31)}$

   (E) $\dfrac{(-2 \times 8.31 \times 3.17)}{1000}$

7. When the equilibrium constant for this reaction is reported in scientific notation, the exponent for 10 is closest to

   (A) −100
   (B) −50
   (C) 0
   (D) +50
   (E) +100

8. Which set of non-standard concentrations does NOT produce a voltage for the cell different from its E° value?

	$[Ag^+]$	$[Mg^{2+}]$
(A)	1.0	1.0
(B)	0.1	0.01
(C)	0.01	0.1
(D)	1.0	0.1
(E)	0.1	1.0

9. For the reaction above in one experiment, the observed value for E is +3.00 V. Which statement(s) apply to this cell?

I. Addition of more oxidizing agent will increase the value of E.
II. Addition of products will decrease the value of E°.
III. As this reaction proceeds, the value of E will decrease and the value of E° will remain the same.

(A) I only
(B) II only
(C) I and II only
(D) I and III only
(E) I, II, and III

Questions 10 and 11: Balance the following equation using redox techniques.

$$\ldots H^+ + \ldots Fe^{2+} + \ldots MnO_4^- \rightarrow \ldots Mn^{2+} + \ldots Fe^{3+} + \ldots H_2O$$

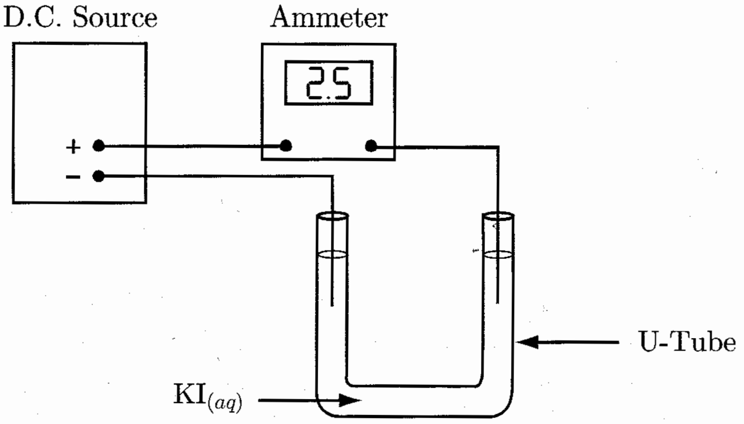
10. What is the sum of the coefficients in this balanced equation?

(A) 6
(B) 8
(C) 16
(D) 22
(E) 24

11. What is the oxidizing agent in this reaction?

(A) H^+
(B) Fe^{2+}
(C) MnO_4^-
(D) Mn^{2+}
(E) Fe^{3+}

Questions 12-15: The diagram below represents apparatus that can be used in the laboratory for the electrolysis of a 1.0 *M* solution of KI. A few drops of phenolphthalein solution are added. The terminals of the 12 volt DC power supply have been labeled with the appropriate charges. The current is supplied at the rate of 2.5 amperes.



12. Which describes the appearance of the contents of the U-tube after the reaction has proceeded for a few minutes?

	anode chamber	**cathode chamber**
(A)	colorless	pink
(B)	brown	pink
(C)	brown	colorless
(D)	pink	colorless
(E)	colorless	colorless

13. Which describes the behavior of $K^+_{(aq)}$ ions in this system?

(A) $K^+_{(aq)}$ ions migrate, as spectator ions, toward the cathode.

(B) $K^+_{(aq)}$ ions migrate toward the anode where they become oxidized to $K_{(s)}$.

(C) $K^+_{(aq)}$ ions migrate toward the anode where they become reduced to $K_{(s)}$.

(D) $K^+_{(aq)}$ ions migrate toward the cathode where they become oxidized to $K_{(s)}$.

(E) $K^+_{(aq)}$ ions migrate toward the cathode where they become reduced to $K_{(s)}$.

14. Which best describes the behavior in the chamber containing the electrode at which bubbles of gas are observed?

(A) $O_{2(g)}$ is produced as the pH of the solution increases.

(B) $O_{2(g)}$ is produced as the pH of the solution decreases.

(C) $H_{2(g)}$ is produced as the pH of the solution increases.

(D) $H_{2(g)}$ is produced as the pH of the solution decreases.

(E) $O_{2(g)}$ is produced as the pH of the solution remains the same.

15. Which expression gives the time in hours needed to produce 0.10 mol $I_{2(aq)}$?

(A) $\dfrac{0.10 \times 2}{2.5 \times 60}$

(B) $\dfrac{0.10 \times 96{,}500}{2.5 \times 60 \times 60}$

(C) $\dfrac{0.10 \times 2}{2.5 \times 60 \times 96{,}500}$

(D) $\dfrac{0.10 \times 2 \times 96{,}500}{2.5 \times 60 \times 60}$

(E) $\dfrac{0.10 \times 2 \times 96{,}500 \times 60}{2.5}$

---

16. In the reaction:

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow 5S + 2MnSO_4 + K_2SO_4 + 8H_2O$$

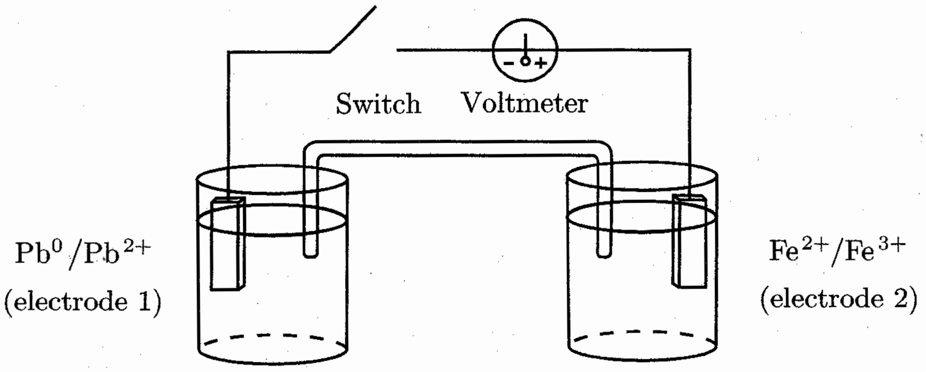
the oxidation number of sulfur changes from

(A) 0 to −2
(B) +5 to −5
(C) −2 to 0
(D) −5 to +5
(E) +6 to +4

Questions 17-20: The diagram below represents a standard Fe^{2+}/Fe^{3+} half cell connected to a standard Pb^0/Pb^{2+} half cell using a salt bridge and an external circuit. The electrodes are numbered for purposes of identification.

$$Pb^{2+}{}_{(aq)} + 2e^- \rightarrow Pb^0{}_{(s)} \qquad E° = -0.13 \text{ volts}$$

$$Fe^{3+}{}_{(aq)} + e^- \rightarrow Fe^{2+}{}_{(aq)} \qquad E° = +0.77 \text{ volts}$$



17. Which describes materials used for the construction of the standard Fe^{2+}/Fe^{3+} half cell?

I. The electrode is made of iron metal.
II. The source of Fe^{2+} could be $Fe(OH)_2$.
III. The source of Fe^{3+} could be $Fe(NO_3)_3$.

(A) I only
(B) III only
(C) II and III only
(D) I and III only
(E) I, II, and III

18. Which gives the changes in masses of the electrodes that occur during operation of the cell?

	mass of electrode #1	**mass of electrode #2**
(A)	decreases	increases
(B)	decreases	remains the same
(C)	remains the same	decreases
(D)	increases	remains the same
(E)	remains the same	increases

19. Which expression gives the value of the standard potential for the cell in volts?

(A) $0.77 - 0.13$
(B) $0.77 + 0.13$
(C) $0.77 + (2 \times 0.13)$
(D) $0.77 - (2 \times 0.13)$
(E) $0.77 + (2 \times (-0.13))$

20. Which gives the value for the potential of the cell in volts if $[Fe^{2+}]$ were changed from standard concentration to 0.010 M?

(A) $E° - 0.0592$
(B) $E° + 0.0592$
(C) $E° + \frac{0.0592}{2}$
(D) $E° - (2 \times 0.0592)$
(E) $E° + (2 \times 0.0592)$

21. The order of chemical activity of three metals is X > Y > Z. Which describes the behavior of these metals?

I. Atoms of X can reduce atoms of Z.
II. Atoms of X can reduce cations of Z.
III. Atoms of Y can reduce cations of X.

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

22. Which gives the best description of ionic concentrations in the standard half-cell based on the half-reaction below?

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)} \qquad E^\circ = 0.22 \text{ volts}$$

(A) $[Ag^+] = [Cl^-] = 1.0\ M$
(B) $[Ag^+] = [Cl^-] < 1.0\ M$
(C) $[Ag^+] = [Cl^-] > 1.0\ M$
(D) $[Cl^-] = 1.0\ M$; $[Ag^+] > [Cl^-]$
(E) $[Cl^-] = 1.0\ M$; $[Ag^+] < [Cl^-]$

23. When the value of E° for a standard galvanic cell is greater than zero, which ranges apply to ΔG° and K_{eq} for the cell reaction?

	ΔG°	K_{eq}
(A)	< 0	> 1
(B)	< 0	< 0
(C)	> 0	> 1
(D)	< 0	> 0 but < 1
(E)	> 0	> 0 but < 1

24. Which describes the oxidation number of nitrogen in each ion of NH_4NO_3?

(A) Both nitrogen atoms have the same oxidation number with the same sign.
(B) Both nitrogen atoms have the same oxidation number with the opposite sign.
(C) The oxidation numbers of the two nitrogen atoms are +4 and +6, respectively.
(D) The oxidation numbers of the two nitrogen atoms are −3 and +5, respectively.
(E) The oxidation numbers of the two nitrogen atoms are −4 and +6, respectively.

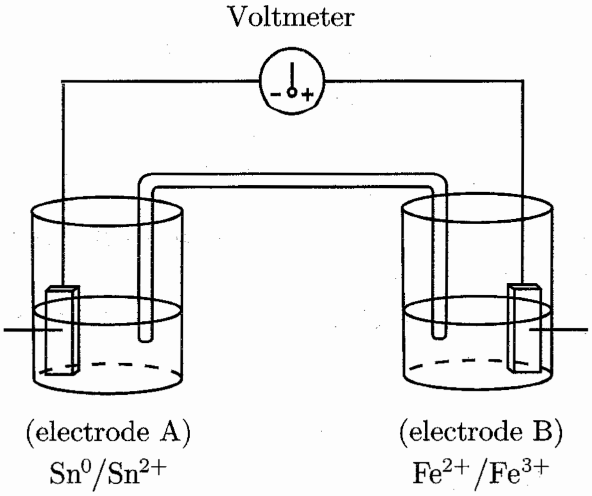
25. A balanced half-reaction must illustrate conservation of

I. charge
II. atoms
III. molecules

(A) I only
(B) I and II only
(C) II only
(D) II and III only
(E) I, II, and III

Free-Response Questions

26. A voltaic cell is set up prepared by connecting a standard Fe^{2+}/Fe^{3+} half cell to a standard Sn^0/Sn^{2+} half cell as shown below. Each half-cell contains 500 mL of 1.0 *M* solution.



(A) Write the overall net equation for this cell reaction and determine the initial cell voltage. Include the appropriate half-reactions and their electrode potentials.

(B) Identify the substance used as electrode A and the substance used as electrode B.

(C) Identify a substance suitable for use as a solute for the solution in the salt bridge. Explain the basis for your choice.

(D) In which direction do electrons flow in the external circuit? Explain.

(E) If 500 mL of water is added to the specified component(s) in the cell, what, if any, is the effect on the reduction potential, E, in each case below? Explain.

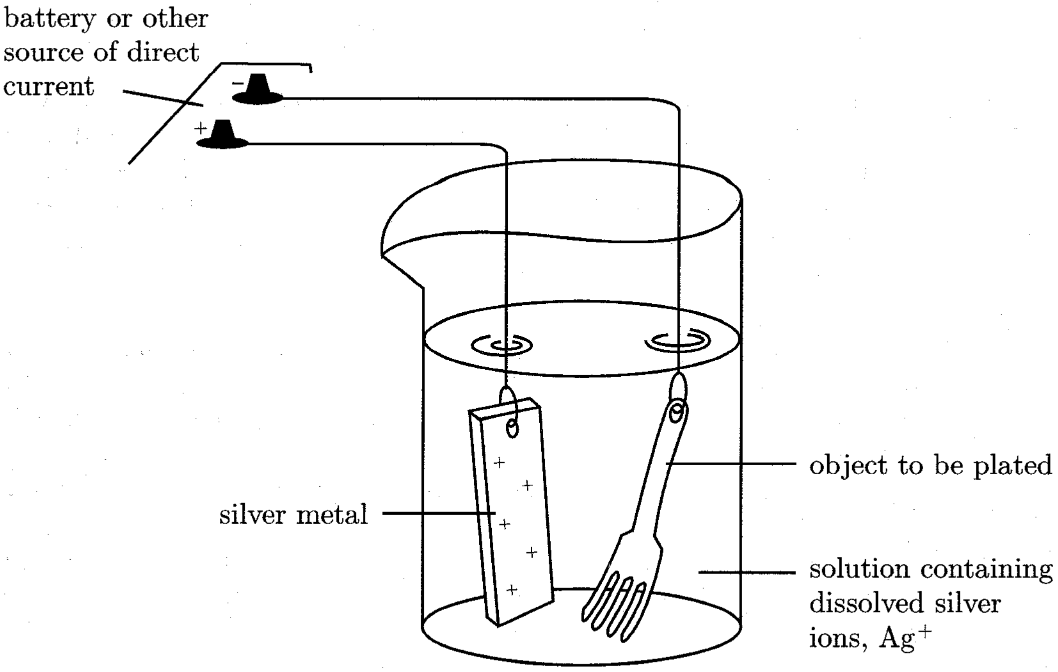
(1) E of the Fe^{2+}/Fe^{3+} half cell, when 500 mL of water is added to that half-cell

(2) E of the Sn^0/Sn^{2+} half cell, when 500 mL of water is added to that half-cell

(3) overall E of the cell, when 500 mL of water is added to each half-cell

(F) What is the cell voltage when the system with the set of standard half-cells has operated long enough so that the concentration of Sn^{2+} has changed by 0.25 *M*?

27. The electrolytic cell shown below is used to plate silver metal onto a fork. Silver metal bars, solid silver nitrate and water are available for use in the cell.



(A) Write the equation for the oxidation half-reaction that occurs in this system. What name is given to any electrode at which oxidation occurs?

(B) What mass of silver metal can be plated onto the spoon using a 30.0 amp current for 60.0 minutes?

(C) What effect is observed on the concentration of $Ag^+{}_{(aq)}$ in this system as the plating proceeds? Explain. (Assume excess mass for the silver metal bar.)

(D) A similar electrolytic device can be used to reduce $H^+{}_{(aq)}$ to $H_{2(g)}$. What volume of $H_{2(g)}$ measured at 298 K and 0.97 atm is produced if the number of faradays as used in part B is used in this similar device?

28. Answer the following questions about the analysis of iron-containing compounds using potassium permanganate solution.

(A) Write the balanced equation in ACID solution for the reaction below:

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

(B) To standardize a potassium permanganate solution, a 0.250 g sample of FAS (iron(II) ammonium sulfate hexahydrate; molar mass: 342 g) is dissolved in 25.00 mL distilled water, then acidified with sulfuric acid. The solution is then titrated with 35.00 mL potassium permanganate solution from a buret until a pale persistent purple color is attained. Calculate the molarity of the potassium permanganate solution.

(C) The standardized potassium permanganate solution is then used to titrate a solution made by dissolving a 0.500 gram sample of a mixture of iron(II) sulfate and sodium sulfate in 50.00 mL dilute sulfuric acid. A total of 10.21 mL of potassium permanganate solution is required to reach the pale purple endpoint. What is the mass percent of iron(II) sulfate in the original mixture?

(D) What would be the effect, if any, on the value for the reported standard molarity of potassium permanganate if the following errors were made? Explain each of your three answers.

(1) Some drops of water remained in the buret after cleaning but before the permanganate solution was added to the buret.

(2) The student neglected to run some permanganate solution through the tip of the buret before taking the initial reading.

(3) The student's lab partner spilled some FAS after weighing it but before titration.

CHAPTER 11

ORGANIC CHEMISTRY

Organic chemistry identifies the branch of chemistry that deals with most compounds of carbon. In AP chemistry, this refers to the study of several homologous series of hydrocarbons and their derivatives based on characteristic functional groups. The chemical and physical properties of these compounds as well as their nomenclature and molecular structure is included in this study.

You are expected to "know" a certain amount of information about organic chemistry. A good mental organization for this information can be based on this simple outline:

Compounds

- Hydrocarbons: names, formulas and properties
- Hydrocarbon derivatives: names, formulas and properties
- Structural formulas, Lewis structures, and isomers for the compounds specified above

Reactions

- Reactions from seven important categories

Much of the information "makes sense" based on molecular structure and related properties. Other information must simply be (ugh!) memorized.

HOMOLOGOUS SERIES OF HYDROCARBONS

You must be able to name and write molecular and structural formulas (Lewis structures) for a wide variety of hydrocarbons and their derivatives. Use this information to provide examples of substances, molecular structures and chemical reactions.

Alkanes

General formula: C_nH_{2n+2};

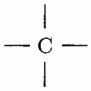
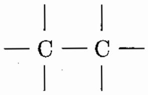
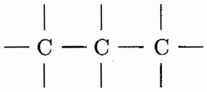
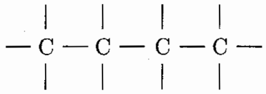
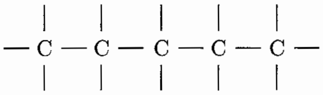
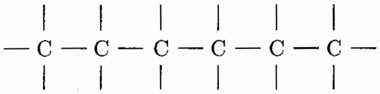
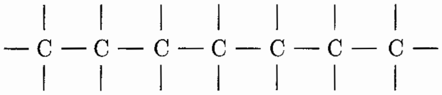
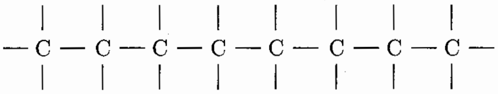
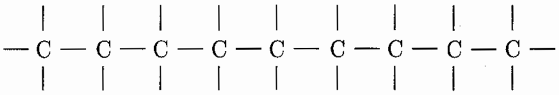
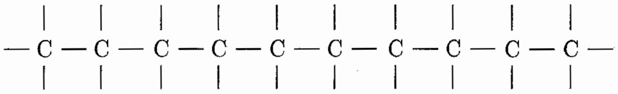
Name: prefix associated with number of carbon atoms as below plus the suffix -*ane*

Bonding: saturated: all carbon-carbon bonds are single bonds; *sp*^{3} hybridization with tetrahedral geometry at each carbon atom

Typical reactions: (note: equations may not be balanced, intentionally)

$$\text{substitution: } C_3H_8 + Cl_2 \rightarrow C_3H_7Cl + HCl$$

$$\text{combustion: } C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$$

Formula	Name	Structural Formula
CH_4	methane	 $-\overset{\vert}{\underset{\vert}{C}}-$
C_2H_6	ethane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_3H_8	propane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_4H_{10}	butane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_5H_{12}	pentane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_6H_{14}	hexane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_7H_{16}	heptane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_8H_{18}	octane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
C_9H_{20}	nonane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
$C_{10}H_{22}$	decane	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$

Alkenes

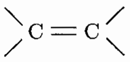
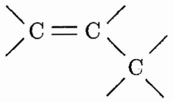
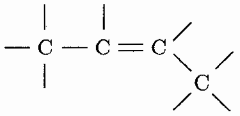
General formula: C_nH_{2n}

Name: prefix associated with number of carbon atoms as above plus the suffix -*ene*

Bonding: unsaturated: one carbon-carbon double bond with sp^2 hybridization (one *sigma* and one *pi* bond) and trigonal planar geometry at each "end" of the double bond; all other carbon-carbon bonds are single bonds.

Typical reaction

addition: $C_4H_8 + Br_2 \rightarrow C_4H_8Br_2$

Formula	**Name**	**Structural formula**	
C_2H_4	ethene		
C_3H_6	propene		
C_4H_8	butene		(2-butene)

(Alkenes with more than four carbon atoms are rarely tested.)

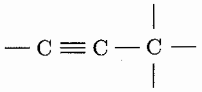
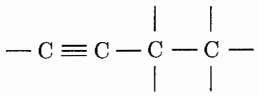
Alkynes

General formula: C_nH_{2n-2}

Name: prefix associated with number of carbon atoms as below plus suffix -*yne*

Bonding: one carbon-carbon triple bond (*sp* hybridization and linear geometry at each "end" of the triple bond); all other carbon-carbon bonds are single bonds.

Typical reaction: addition: $C_4H_6 + Br_2 \rightarrow C_4H_6Br_4$

Formula	**Name**	**Structural formula**	
C_2H_2	ethyne	$-C \equiv C-$	
C_3H_4	propyne	 $-C \equiv C - \underset{\vert}{\overset{\vert}{C}} -$	
C_4H_6	butyne	 $-C \equiv C - \underset{\vert}{\overset{\vert}{C}} - \underset{\vert}{\overset{\vert}{C}} -$	(1-butyne)

(Alkynes with more than four carbon atoms are rarely tested.)

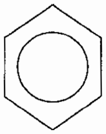
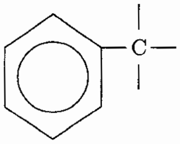
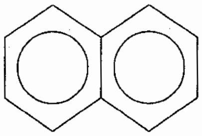
Aromatic Hydrocarbons: the benzene series

General formula: C_nH_{2n-6}

Name: C_6H_6 - benzene; $C_6H_5CH_3$ - toluene;
$C_{10}H_8$ - naphthalene - actually two benzene "rings" sharing one side of their hexagons

Bonding: resonance structures; behaves more like a saturated compound than unsaturated; six carbon ring with **six sets of** sp^2 hybrid orbitals (six *sigma* bonds) and six delocalized (resonance) electrons equivalent to three *pi* bonds

Typical reactions: substitution: $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

Formula	**Name**	**Structural Formula**
C_6H_5	benzene	
$C_6H_5CH_3$	toluene	
$C_{10}H_8$	naphthalene	

FUNCTIONAL GROUPS AND HYDROCARBON DERIVATIVES

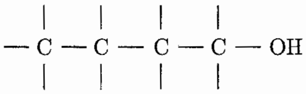
Alcohols

primary alcohol

secondary alcohol

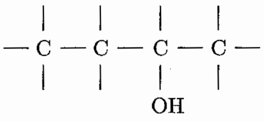
tertiary alcohol

R-CH_2OH



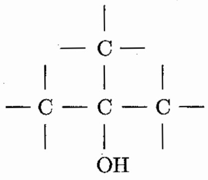
1-butanol
(primary)

R-CHOH-R'



2-butanol
(secondary)

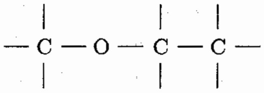
R- R'- R''- OH



2-methyl-2-propanol
(tertiary)

Ethers

R – O - R'

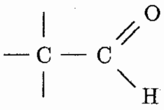


$-C-O-C-C-$

methyl ethyl ether

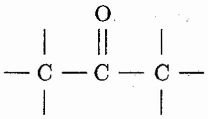
Aldehydes & Ketones

R – CHO



propanal

R – CO – R'

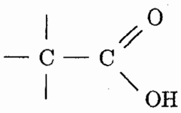


$-C-\overset{\overset{O}{\|}}{C}-C-$

propanone

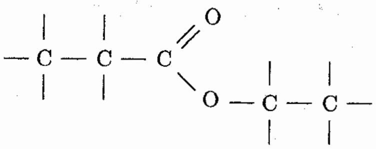
Carboxylic acids and esters

R – COOH



ethanoic acid

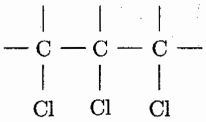
R – COO – R'



ethyl propanoate

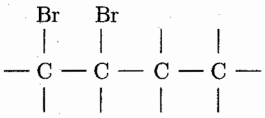
Halohydrocarbons

R – X



$-\underset{Cl}{C}-\underset{Cl}{C}-\underset{Cl}{C}-$

1,2,3-trichloropropane

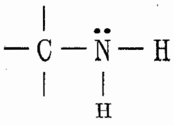


$-\overset{Br}{C}-\overset{Br}{C}-C-C-$

1,2-dibromobutane

Amines

R – NH_2



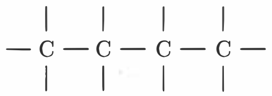
$-C-\underset{H}{\ddot{N}}-H$

methyl amine

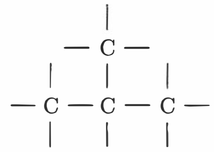
ISOMERISM: STRUCTURAL, *CIS-TRANS*, OPTICAL

You need to become familiar with simple illustrations of isomerism. Two compounds are isomers of each other when they have the same molecular formula but different structural formulas. Sometimes recognition and naming is sufficient. At other times, you will need to draw Lewis structures as well as assign names. Since isomers have different structures, they are likely to have different chemical and physical properties.

Structural isomerism:

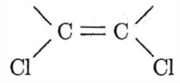


butane

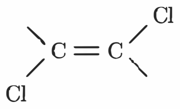


2-methylpropane

Cis-trans isomerism: $C_2H_2Cl_2$

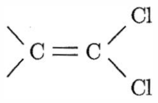


cis-1,2-dichloroethene

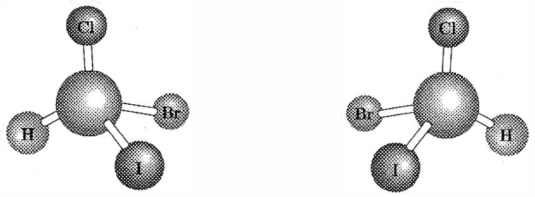


trans-1,2-dichloroethene

See also 1,1-dichloroethene, below, a structural isomer.



Optical isomerism: (enantiomers)



CHClBrI

two mirror images that cannot be superimposed

ORGANIC REACTIONS

Every reaction is simply a statement of a chemical property; that is, how one substance behaves in the presence of another when there is sufficient energy to start the reaction. Figure 11.1 provides a useful summary of some common organic reactions. Some organic reactions are slow starters with high energies of activation. For example, there is no reaction between gasoline and air (oxygen) until a spark is provided.

Compared to inorganic reactions in water solution, reactions between organic compounds generally proceed at much lower rates. Unlike charged ions, these neutral molecules have no special attraction for each other.

Figure 11.1 Some common organic reactions

	Reactants	Principal organic product
Substitution	saturated hydrocarbon + halogen, X_2	halohydrocarbon + HX
Addition	unsaturated hydrocarbon + halogen, X_2	halohydrocarbon
Esterification	carboxylic acid + alcohol	ester + HOH
Combustion	hydrocarbon + oxygen	CO_2 (or CO) + HOH
Oxidation	alcohol + oxidizing agent	aldehyde, ketone or acid
Polymerization **Addition Polymerization**	small unsaturated monomers	large saturated polymer
Condensation Polymerization	small monomers	large polymer and water or similar small molecules

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

IV. Descriptive Chemistry

3. introduction to organic chemistry: hydrocarbons and functional groups (structure, nomenclature, chemical properties)

see also the section on Chemical Bonding (I.B.3): structural isomerism of simple organic molecules

from the list of CHEMICAL CALCULATIONS

No special calculations are associated with organic chemistry.

from the list of EQUATIONS & CONSTANTS

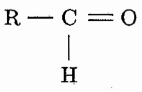
No entries are related specifically to organic chemistry.

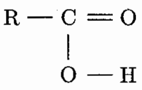
from the list of RECOMMENDED EXPERIMENTS

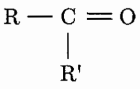
22. Synthesis, purification and analysis of an organic compound

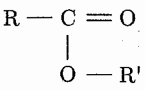
Multiple Choice Questions

Questions 1-5: The set of lettered choices is a list of functional groups found in organic compounds. Questions numbered 1–5 identifies some categories of organic compounds. For each numbered category, choose the functional group from the lettered list with which it is most closely associated.

(A)

$R-\underset{\underset{\displaystyle H}{|}}{C}=O$

(B)

$R-\underset{\underset{\displaystyle O-H}{|}}{C}=O$

(C)

$R-\underset{\underset{\displaystyle R'}{|}}{C}=O$

(D)

$R-\underset{\underset{\displaystyle O-R'}{|}}{C}=O$

(E) $R-OH$

1. alcohol

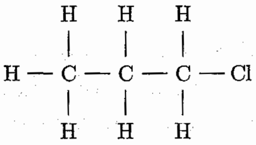
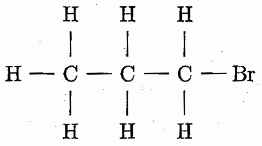
2. carboxylic acid

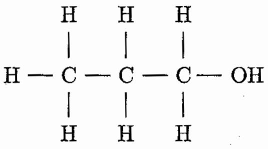
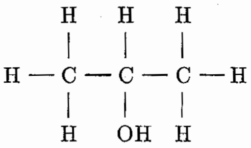
3. ketone

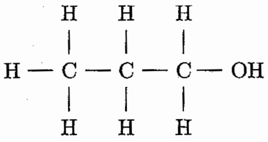
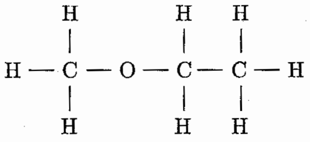
4. ester

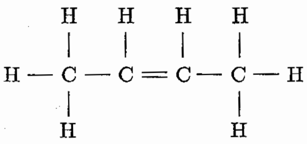
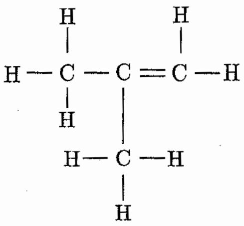
5. aldehyde

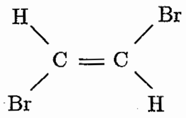
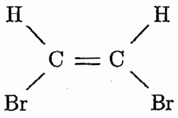
6. Each of the following illustrates a pair of isomers EXCEPT

(A)  and 

(B)  and 

(C)  and 

(D)  and 

(E)  and 

7. Which organic compound is a weak electrolyte?

(A) C_2H_6

(B) CH_3Cl

(C) HCOOH

(D) CH_3OH

(E) $C_6H_{12}O_6$

8. In the fermentation of plant materials, which kind of compound is converted to alcohol?

(A) acid

(B) enzyme

(C) carbonate

(D) carbohydrate

(E) hydrocarbon

9. Which is the best description of the bonding associated with carbon atoms in most organic compounds?
   (A) formation of negative carbanions
   (B) formation of positive carbonium ions
   (C) formation of carbon free radicals with seven electrons
   (D) contribution of four electrons to the sharing of four pairs of electrons
   (E) transfer of electrons from carbon to elements with higher electronegativity

10. Which alcohol reacts with ethanoic acid to produce a four-carbon ester?
   (A) butanol
   (B) ethanol
   (C) methanol
   (D) pentanol
   (E) propanol

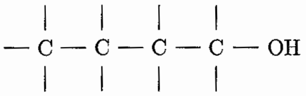
11. What is the total number of electron pairs shared between carbon atoms in a molecule of propene?
   (A) two
   (B) three
   (C) four
   (D) five
   (E) none

12. Which of the five compounds listed below has a molar mass that is different from the other four?
   (A) 2-butanol
   (B) 2-propanol
   (C) diethyl ether
   (D) 2-methyl-2-propanol
   (E) 2-methyl-1-propanol

13. Which of the following compounds represents the greatest degree of oxidation?
   (A) organic acid
   (B) ketone
   (C) alcohol
   (D) aldehyde
   (E) hydrocarbon

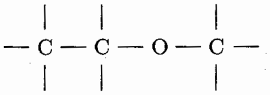
14. Which is an isomer of diethyl ether, $C_2H_5OC_2H_5$?

(A) C_4H_9OH



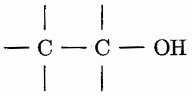
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH$

(B) $C_2H_5OCH_3$



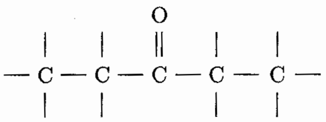
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$

(C) C_2H_5OH



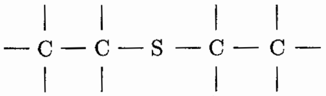
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH$

(D) $C_2H_5COC_2H_5$



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$

(E) $C_2H_5SC_2H_5$



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$

15. Which type of organic compound is most likely to participate in an addition reaction?

(A) acid
(B) alcohol
(C) aldehyde
(D) alkene
(E) ester

16. A molecule of ethene is similar to a molecule of methane in that they both have the same

(A) structural formula
(B) molecular formula
(C) number of carbon atoms
(D) number of carbon-carbon bonds.
(E) number of hydrogen atoms

17. The compound, 2-methylpentane, is an isomer of

(A) pentane
(B) 2-methylbutane
(C) 2,2-dimethylbutane
(D) 2,2-dimethylpentane
(E) 2,2-dimenthylpropane

18. When $KMnO_4$ reacts with ethanol in acid solution, manganese becomes

(A) ionized
(B) oxidized
(C) reduced
(D) catalyzed
(E) dehydrated

19. Among the processes used to refine petroleum, which is most closely associated with differences in vapor pressure?

(A) osmosis
(B) filtration
(C) distillation
(D) crystallization
(E) centrifugation

20. Which is a correct comparison of carbon-carbon single bonds to carbon-carbon double bonds in hydrocarbon molecules?

I. The bond length of the single bond is greater.
II. The bond energy of the single bond is greater.
III. The reactivity of the single bond is greater.

(A) I only
(B) III only
(C) I and II only
(D) II and III only
(E) I, II, and III

21. Which formula represents an unsaturated hydrocarbon?

(A) C_3H_6
(B) C_3H_8
(C) $C_2H_5CH_2OH$
(D) C_2H_5CHO
(E) C_2H_5COOH

22. A 1.0 molal aqueous solution of methanol differs from a 1.0 molal aqueous solution of acetic acid in that the aqueous solution of methanol
    (A) contains two phases
    (B) has a higher density
    (C) conducts electricity
    (D) turns blue litmus to red
    (E) contains only molecules

23. What is the total number of shared electron pairs between all adjacent carbon atoms in a propyne molecule?
    (A) 1
    (B) 2
    (C) 3
    (D) 4
    (E) 5

24. Which hybridization provides the best explanation for the geometry of the *sigma* (σ) bonds in formaldehyde, HCHO?
    (A) sp
    (B) sp^2
    (C) sp^3
    (D) dsp^3
    (E) d^2sp^3

25. Which general formula applies to hydrocarbons with one double covalent bond between adjacent carbon atoms?
    (A) C_nH_{2n+2}
    (B) C_nH_{2n}
    (C) C_nH_{2n-2}
    (D) C_nH_{2n-4}
    (E) C_nH_{2n-6}

Free-Response Questions

26. Use principles of chemical bonding to answer the following questions about several organic compounds.

    (A) Write the structural formulas and the IUPAC name for each of the two isomers of $C_2H_4Br_2$.

    (B) Which of the two isomers has the greater polarity? Explain.

    (C) Write labeled structural formulas to show the difference in bonding between methyl ethanoate and ethyl methanoate.

    (D) The value of K_a for the aromatic acid, phenol, C_6H_5OH, is 1.3×10^{-10}. The value of K_a for the carboxylic acid, ethanoic acid, CH_3COOH, is 1.8×10^{-5}. Using this information, discuss the difference in bond strength for the O–H bond in each substance.

27. Consider the formulas of the organic compounds listed below

    C_2H_6 $C_2H_2Br_2$ C_2H_5OH CH_3COOH $CHClBrI$ C_4H_9OH

    (A) Choose the formula of the substance above whose molecules contain one carbon-carbon double bond. Write the names and structural formulas of its *cis* and *trans* isomers.

    (B) Choose the formulas of the two substances above that react to form an ester. Write the name and structural formula of that ester.

    (C) Choose the formula of the substance above that donates a proton most readily to OH^- in water solution. Write the name and structural formula of that proton donor.

    (D) Choose the formula of the substance above whose molecules exhibit optical isomerism. Write a pair of structural formulas to illustrate that isomerism.

    (E) Choose the formula of the alcohol that exists as four isomers. Name and draw the structural formula for each of the four isomers.

28. For each of the following, name the category of reaction that occurs and write the structural formula for the principal organic product.

    (A) C_4H_9OH is mixed with CH_3COOH in the presence of concentrated H_2SO_4.

    (B) $Br_{2(\ell)}$ is added to *cyclo*-C_6H_{10}.

    (C) A solution of $KMnO_4$ is added to an acidified solution of C_3H_7OH.

    (D) C_2H_4 is heated in the presence of a catalyst.

CHAPTER 12

DESCRIPTIVE CHEMISTRY

"Descriptive chemistry" is a nebulous term that might be interpreted to include any chemistry that is non-quantitative. Much of "descriptive chemistry" addresses the physical and chemical properties of various elements and compounds. Those properties include the interactions of these various elements and compounds with each other. Other information may also be included in "descriptive chemistry". For example, nuclear chemistry might be considered a descriptive topic within the AP Chemistry arena. You may be asked to write and balance nuclear equations and to describe how nuclear changes proceed. In addition, half-life problems from reaction kinetics are frequently presented in nuclear chemistry terms. Much of what you are expected to know can be gleaned from your first-hand experiences in the laboratory. How better to learn that copper(II) ion is blue in aqueous solution or that zinc metal reacts vigorously with strong acid to produce hydrogen gas? Be absolutely sure to review your laboratory notebook before taking the AP Chemistry examination!

WRITING NET IONIC EQUATIONS: ALWAYS ELIMINATE SPECTATOR IONS!

One question in the free response section of the AP Chemistry examination always requires you to write net ionic equations to demonstrate your knowledge of chemical changes. You have already addressed this topic thoroughly in the introductory section of this book. The products of many of these reactions can be predicted by a qualitative background in descriptive chemistry. In your reaction, be sure to show the formula for any species that is present

- as a dissolved ion that undergoes chemical change
- in solid, liquid or gaseous phase
- as a molecular species

Spectator ions (those ions that exist in the same form on both reactant and product side of a complete ionic equation) must be eliminated since they have not participated in any chemical change.

Periodic Table (See also Chapter 1.)

Be sure that you can identify and locate the representative (main group) elements, active metals, transition metals, inner transition metals (rare earth elements), metalloids, nonmetals, and noble gases. You should be able to write convincingly about their chemical behavior and electron configuration as well as the relationship between those two characteristics. Periodic trends in several properties are frequently addressed on the AP Exam. The summary below is a reminder of the principles discussed in Chapter 1.

Periodic Trends

Within a period, as atomic number increases:

- atomic radius decreases
- first ionization energy increases
- electron affinity becomes more negative
- ionic radius for isoelectronic species decreases
- melting point decreases

Within a group, as atomic number increases:

- atomic radius increases
- first ionization energy decreases
- ionic radius increases
- melting point increases

ACIDS, BASES, AND SALTS (See also Chapter 9.)

You should know the names and formulas of the common acids that are classified as strong because they dissociate completely in solution (HCl, HBr, HI, $HClO_4$, HNO_3, H_2SO_4). All other acids (species that can donate a proton in water solution) are considered to be weak. The relative strengths of these weak acids can be compared by referring to their K_a values. When you compare the strength of oxyacids that are identical except for the number of oxygens included, the molecule with more oxygen atoms is the stronger acid ($HNO_3 > HNO_2$; $H_2SO_4 > H_2SO_3$). If oxyacids are similar except for the central non-metal atom, the acid with the non-metal of greater electronegativity is the stronger acid ($H_2SO_4 > H_2SeO_4$).

The strong bases are the hydroxides of all Group 1 metals and the heavier Group 2 metals such as $Ba(OH)_2$ and $Sr(OH)_2$; some authorities include $Ca(OH)_2$. All other hydroxides and proton acceptors are considered to be weak bases.

Acidic and basic anhydrides are oxides that react with water to form easily recognized acids or bases. Oxides of non-metals are acid anhydrides (SO_2 forms H_2SO_3; SO_3 forms H_2SO_4). Oxides of metals are basic anhydrides (Li_2O forms $LiOH$; BaO forms $Ba(OH)_2$). Note that there is no change in the oxidation number of the non-metal or metal element when the oxide dissolves in water to form the acid or the base. When anhydrides react with water, there is no oxidation or reduction. An acid anhydride combines with a basic anhydride to form a salt ($CaO + SO_3 \rightarrow CaSO_4$). Note that even though there is no water is in sight, the reaction can still be considered an acid-base reaction!

Solutions of salts in water: hydrolysis

Recall that some salts dissolve in water to form acidic or basic solutions. See Chapter 9 for the discuşsion of hydrolysis. The information below can be used to predict the acidity of most salt solutions:

Salts of strong acid & weak base → acidic solution;
eg. $FeCl_3$ - a salt derived from HCl, a strong acid, and $Fe(OH)_3$, a weak base

Salts of weak acid & strong base → basic solution;
eg. K_2CO_3 - a salt derived from H_2CO_3, a weak acid, and KOH, a strong base

Salts of strong acid & strong base → neutral solution;
eg. Na_2SO_4 - a salt derived from H_2SO_4, a strong acid, and NaOH, a strong base

Salts of weak acid & weak base → nature of solution not easily predicted

Colors of solutions

You may be asked to discuss the presence or absence of certain ions in solution based on information about color. See Figure 12.1 for a list of ions often used in AP Chemistry.

Figure 12.1 Colors of ions in aqueous solution

ion	color
Cu^{2+}	blue
Ni^{2+}	green
CrO_4^{2-}	yellow
$Cr_2O_7^{2-}$	orange
MnO_4^-	violet
Co^{2+}	pink
Fe^{3+}	pale yellow

In general, the presence of unpaired *d*-sublevel electrons is associated with colored precipitates/solutions/or gases. Otherwise, products are likely to be white or colorless in solution.

OXIDIZING AND REDUCING AGENTS (See also Chapter 10.)

Be able to identify common oxidizing and reducing agents in order to discuss oxidation-reductions reactions. See Figure 12.2 (below). You should always look for species that contain atoms that have been pushed to an extreme in either accepting or donating electrons. For example, the oxidation number of the manganese atom in permanganate MnO_4^- is +7. It has already "lost" all seven *4s* and *3d* electrons that it was assigned as a free atom; it has no more valence electrons to lose. Permanganate can only be reduced by gaining electrons and therefore is a vigorous oxidizing agent. For similar reasons, chromate and dichromate, where ON for chromium is +6, are also excellent oxidizing agents.

Species that are in the middle of their possible range of oxidation numbers can be either oxidized or reduced, depending on the context. Thus hypochlorite, ClO^-, can be reduced to chlorine, Cl_2, or oxidized to chlorite, ClO_2^-, depending on the relative strength of its redox partner.

Figure 12.2 Commonly used oxidizing and reducing agents

Common oxidizing agents and their reduction products:

$MnO_4^- \rightarrow Mn^{2+}$ (acidic); MnO_2, occasionally MnO_4^{2-} (basic)

$NO_3^- \rightarrow NO_2$, NO or NH_4^+ (acidic)

$H_2O_2 \rightarrow H_2O$ (acidic)

$H_2SO_4 \rightarrow SO_2$ (acidic)

Active nonmetals → anions (such as $Br_2 \rightarrow Br^-$)

Common reducing agents and their oxidation products:

$SO_2 \rightarrow SO_4^{2-}$

$SO_3^{2-} \rightarrow SO_4^{2-}$

$Sn^{2+} \rightarrow Sn^{4+}$

Active metals → cations (such as $Ba \rightarrow Ba^{2+}$)

ORGANIC CHEMISTRY (See also Chapter 11.)

Organic chemistry is the study of most of the compounds that contain carbon atoms. Molecules that contain only carbon atoms and hydrogen atoms are called hydrocarbons. You should know how to identify and name three series of hydrocarbons, the alkanes, alkenes, and alkynes and their derivatives (alcohols, ethers, and so on). Similarly, you should also be familiar with the properties of benzene, C_6H_6, and toluene, $C_6H_5CH_3$. It is also useful to know a handful of important reactions. See Chapter 11 for a review of this information. Physical and chemical properties of simple organic compounds should be included as exemplary material for the study of other areas such as bonding, equilibria involving weak acids and bases, kinetics, colligative properties, and stoichiometric determinations of empirical and molecular formulas. It is not necessary to conduct an in-depth survey of organic chemistry at this point since a successful performance on the AP Chemistry examination tends to point you towards a full-fledged course in organic chemistry anyway!

COORDINATION COMPOUNDS

Although coordination chemistry is a fascinating topic in its own right, it is not a major topic of the AP Chemistry course. The bonding is interesting as ligands donate a pair of electrons from a filled orbital of the ligand to an empty orbital in the central metal cation to form a coordinate covalent bond. You should be able to name coordination compounds by identifying and naming the complex ion, then pairing it with another ion to complete the compound. You should also be familiar with the geometry of shared electron pairs (see Chapter 2) and with isomer formation based on location of ligands. These compounds may show spectacular colors so it is well worth your time in lab to synthesize such a compound. A list of common ligands is given in Fig 12.3.

Figure 12.3 Common ligands and nomenclature

Ligand	Name
NH_3	ammine- (note spelling, two "m"s)
CN^-	cyano-
H_2O	aqua- (occasionally, aquo-)
OH^-	hydroxy-
Cl^-	chloro-
$C_2O_4{}^{2-}$	oxalato- (a bidentate ligand - two electron pairs available for sharing)

Naming Coordination Compounds

1. In a compound, the cation is named first, then the anion.
2. In a complex ion, the ligands are named first, then the metal cation.
3. Ligands are named by adding -o to the anion name (chloride becomes chloro-, cyanide becomes cyano-, and so on).
4. If there is more than one of a given ligand, the number is denoted by a Greek counting prefix (di-, tri-, tetra-, penta-, etc.). If the name of the ligand already contains a Greek counting prefix, then the prefixes bis-, tris-, tetrakis-, pentakis-, and so on are used instead.
5. The oxidation number of the metal cation is denoted by use of a Stock system Roman numeral in parentheses.
6. If there is more than one type of ligand, they are listed in alphabetical order.
7. If the complex ion is an anion, its name must end in -ate.

Examples:

$[Co(H_2O)_4Cl_2]Br$	tetraaquadichlorocobalt(III) bromide
$[Co(H_2O)_6]^{3+}$	hexaaquacobalt(III) cation
$[CoCl_4]^-$	tetrachlorocobaltate(III) anion

NUCLEAR CHEMISTRY

You should be able to write and balance nuclear equations that include alpha, beta, and positron emission and electron absorption (K-capture). Figure 12.4 contains a list of frequently used symbols. As long as you remember to maintain conservation of charge (the total number of protons on each side of the equation must be the same) and conservation of mass (the total number of protons plus neutrons on each side of the equation must be the same), balancing nuclear equations is easy. The balanced equation below represents the bombardment of an isotope of aluminum with alpha particles.

$$^{4}_{2}\mathrm{He} + {}^{27}_{13}\mathrm{Al} \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n}$$

Chemists frequently do not include gamma radiation in these equations since the high energy gamma rays have neither charge nor mass and therefore do not affect those values.

Radioactive decay is a first-order process. Half-life as discussed in Chapter 6 applies to the radioactive decay of most isotopes.

Figure 12.4

SYMBOLS USED IN NUCLEAR CHEMISTRY		
electron (beta particle)	$^{0}_{-1}\mathrm{e}$	β^-
position	$^{0}_{+1}\mathrm{e}$	β^+
proton	$^{1}_{1}\mathrm{H}$	p
alpha particle	$^{4}_{2}\mathrm{He}$	α
neutron	$^{1}_{0}\mathrm{n}$	n
gamma radiation		γ

from the TOPIC OUTLINE (website: apcentral.collegeboard.com)

I. Structure of Matter

  C. Nuclear chemistry: nuclear equations, half-lives and radioactivity; chemical application

IV. Descriptive Chemistry

  1. Chemical reactivity and products of chemical reactions
  2. Relationships in the Periodic Table: horizontal, vertical and diagonal with examples from alkali metals, alkaline earth metals, halogens, and the first series of transition elements.

from the list of CHEMICAL CALCULATIONS

No calculations are especially associated with Descriptive Chemistry.

from the list of EQUATIONS & CONSTANTS

Beer's law for colored solutions

$$A = abc \text{ where}$$

A = absorbance

a = molar absorptivity

b = path length

c = concentration (molarity)

from the list of RECOMMENDED EXPERIMENTS

14. Separation and qualitative analysis of cations and anions
15. Synthesis of a coordination compound and its chemical analysis
17. Colorimetric or spectrophotometric analysis (see Beer's Law)
18. Separation by chromatography
22. Synthesis, purification, and analysis of an organic compound

Multiple Choice Questions

Questions 1-5: The set of lettered choices below is a list of observations that refer to the numbered list of mixtures immediately following. For each numbered mixture, select the one lettered observation that is most closely associated with the mixture specified. A choice may be used once, more than once or not at all.

(A) forms a colorless solution with a colored precipitate
(B) forms a colorless solution with white precipitate
(C) forms a colored solution with no precipitate
(D) forms a colorless solution only with no precipitate or evolution of gas
(E) forms a solution with no precipitate, accompanied by evolution of gas

1. $CaCl_{2(aq)} + NaCl_{(aq)}$

2. $AgNO_{3(aq)} + KCl_{(aq)}$

3. $K_2CrO_{4(aq)}$ + excess $Ba(NO_3)_{2(aq)}$

4. dilute $HCl_{(aq)} + KHCO_{3(aq)}$

5. $CrCl_{3(s)}$ + dilute $HNO_{3(aq)}$

---

6. Which mixture of solids dissolves completely in dilute hydrochloric acid but not in distilled water?

(A) NaCl and KNO_3
(B) $Ca(NO_3)_2$ and NaCl
(C) Na_2CO_3 and $CaCl_2$
(D) $NaHCO_3$ and $Ca(NO_3)_2$
(E) $Ca(HCO_3)_2$ and KNO_3

7. Which occurs when CO_2 is bubbled into a solution of limewater, $Ca(OH)_2$?

(A) A white precipitate forms that redissolves.
(B) A light blue precipitate accumulates at the top of the mixture.
(C) The liquid separates into two immiscible layers.
(D) A noticeable evolution of energy occurs with a corresponding increase in temperature.
(E) A noticeable absorption of energy occurs with a corresponding decrease in temperature.

Questions 8-12: The set of lettered choices below is a list of ions in separate water solutions that are to be tested with a solution of NaOH. Each of the numbered mixtures immediately following contains NaOH and only one species of ion from those listed. Select the one ion from the list of lettered choices that is most closely associated with the mixture specified. A choice may be used once, more than once or not at all.

(A) Al^{3+}
(B) $Cr_2O_7{}^{2-}$
(C) Mg^{2+}
(D) $NH_4{}^+$
(E) Ni^{2+}

8. When solution of NaOH is added, the color of the solution changes from orange to yellow.

9. When NaOH solution is added and the mixture warmed, the smell of ammonia is detected.

10. When excess NaOH solution is added, a white precipitate forms that redissolves.

11. When NaOH solution is added, a persistent white precipitate forms.

12. When NaOH solution is added, a persistent green precipitate forms.

---

13. Which pair of solutions, when mixed, produces a white precipitate?

(A) $AgNO_3 + NaCl$
(B) $AgNO_3 + K_2CrO_4$
(C) $AgNO_3 + KMnO_4$
(D) $Mn(NO_3)_2 + Na_2S$
(E) $AgNO_3 + Na_2S$

14. Each of the following cations forms a colored aqueous solution EXCEPT

(A) Ca^{2+}
(B) Ni^{2+}
(C) Cu^{2+}
(D) Mn^{2+}
(E) Co^{2+}

Questions 15-19:

(A) Na
(B) S
(C) P
(D) Si
(E) Zn

The set of lettered choices above is a list of chemical elements. For each numbered statement below, select the element that is most closely associated with that statement. A lettered choice may be used once, more than once, or not at all.

15. One of its oxides is a gas that dissolves in water to form a strong acid.

16. Its oxide is a solid that dissolves in water to form a strong base.

17. Its oxide is a network solid that is insoluble in water.

18. Its oxide is a solid that dissolves in both excess acid and excess base.

19. One of its oxides is a white solid that dissolves in water to form a weak acid.

---

20. Which group of the Periodic Table includes elements with names meaning "the Sun element", "the new one", "the lazy one", "the hidden one", and "the strange one"?
    (A) alkali metals
    (B) alkaline earth metals
    (C) chalcogens
    (D) halogens
    (E) noble gases

21. Which gives the correct trend in atomic number and corresponding atomic radius within the third period of the Periodic Table?
    (A) As atomic number increases, the atomic radius decreases.
    (B) As atomic number increases, the atomic radius increases.
    (C) As atomic number increases, the atomic radius remains the same.
    (D) As atomic number remains the same, the atomic radius increases.
    (E) As atomic number remains the same, the atomic radius decreases.

22. Which kind of atom listed below contains the greatest number of unpaired electrons?
    (A) K
    (B) Sc
    (C) V
    (D) Mn
    (E) Co

23. Which describes the gas produced when dilute hydrochloric acid is added to solid sodium hydrogen sulfite, $NaHSO_3$?
    (A) dark brown in color
    (B) turns limewater cloudy
    (C) re-ignites a glowing splint
    (D) has a sharp, choking odor
    (E) has the odor of rotten eggs

24. Which pair gives correct formulas for two different chlorides of iron?
    (A) $FeCl$, $FeCl_2$
    (B) Fe_2Cl_2, $FeCl_2$
    (C) $FeCl_2$, $FeCl_3$
    (D) $FeCl_2$, $FeCl_4$
    (E) $FeCl_3$, $FeCl_4$

25. Which is most soluble in water?
    (A) C_2H_5OH, ethanol
    (B) C_2H_5Cl, chloroethane
    (C) $C_2H_5C_6H_5$, ethyl benzene
    (D) $C_2H_5OC_2H_5$, diethyl ether
    (E) $C_2H_5COOC_2H_5$, ethyl propanoate