SAMPLE EXAMINATION IV

Section I – Multiple Choice

Questions 1-5. The set of lettered choices, a list of oxides, below refers to the numbered phrases immediately following it. Select the one lettered choice that is most closely associated with each numbered phrase. Each lettered choice can be used once, more than once or not at all.

(A) SO_2

(B) BaO_2

(C) CO_2

(D) GeO_2

(E) NO_2

1. an odd electron molecule

2. an ionic compound

3. at STP the gas that illustrates greatest deviation from ideal behavior

4. source of a semiconductor

5. includes a element with oxidation number of +2

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6. Which event is most likely to occur in an experiment to measure ionization energy?

   (A) A positive ion is converted to a negative ion.

   (B) A neutral atom is converted to a positive ion.

   (C) A neutral atom is converted to a negative ion.

   (D) A negative ion is converted to a neutral atom.

   (E) A negative ion is converted to a positive ion.

SAMPLE EXAMINATION IV

Section I – Multiple Choice

Questions 1-5.

1. Because each compound has two oxygen atoms (16 electrons), the correct answer can be determined by referring to the atomic number of the element combined with oxygen as shown below:

   (A) $_{16}S$ (B) $_{56}Ba$ (C) $_{6}C$ (D) $_{32}Ge$ (E) $_{7}N$

   Only nitrogen (choice (E)) has an odd number of electrons. (Note that this characteristic of electron count indicates that no proper Lewis structure can be drawn for NO_2.)

2. Of the compounds listed, only BaO_2 (choice (B)) is the compound of a metal and a nonmetal, indicating an ionic compound. The ions in this compound are the Ba^{2+} ion and the $O_2{}^{2-}$ (peroxide) ion.

3. Of the compounds listed, only SO_2, CO_2 and NO_2 are gases at STP. SO_2 deviates from ideal behavior more than CO_2 or NO_2 because SO_2 has stronger intermolecular forces and a larger electron cloud than either of the other oxides.

4. Of the compounds listed, only GeO_2 (choice (D)) includes a metalloid (semimetal) element. Such elements including Ge are found in semiconductors.

5. In the compounds listed, all the elements combined with oxygen have an oxidation number of +4 except for Ba (choice (B)) which has an oxidation number of +2, equal to its ionic charge. Note that the oxidation number of oxygen in peroxides is -1.

The correct choices are: 1(E) 2(B) 3(A) 4(D) 5(B)

6. Ionization energy is defined by the equation below:

   $$M^0{}_{(g)} + \text{energy} \rightarrow M^+{}_{(g)} + e^-$$

   that is, the energy required to remove the outermost electron from an atom in the gas phase. The product is a positive ion in the gas phase.

   The correct choice is (B).

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

$$\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3}$$

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

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad K_p = P_{CO_2}$$

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

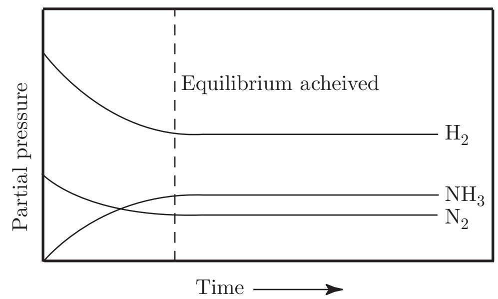
f. buffer solutions

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

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

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

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

$$K_w = [OH^+][H^+] = 1\ 0^{-14} \text{ @ } 25^\circ C$$

$$= K_a \times K_b$$

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

$$14 = pH + pOH$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pOH = pK_b + \log\frac{[HB^+]}{[B]}$$

$$pK_a = -\log K_a,\ pK_b = -\log K_b$$

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

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.

CHAPTER 4
SOLUTIONS

1. Determine $[Cl^-]$ for each sample:

NH_4Cl: $\frac{0.30 \text{ mol solute}}{1 \text{ L solution}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol solute}} = 0.30 \qquad [Cl^-] = 0.30$

NaCl: $\frac{0.10 \text{ mol solute}}{1 \text{ L solution}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol solute}} = 0.10 \qquad [Cl^-] = 0.10$

KCl: $\frac{0.20 \text{ mol solute}}{1 \text{ L solution}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol solute}} = 0.20 \qquad [Cl^-] = 0.20$

$MgCl_2$: $\frac{0.20 \text{ mol solute}}{1 \text{ L solution}} \times \frac{2 \text{ mol } Cl^-}{1 \text{ mol solute}} = 0.40 \qquad [Cl^-] = 0.40$

$FeCl_3$: $\frac{0.10 \text{ mol solute}}{1 \text{ L solution}} \times \frac{3 \text{ mol } Cl^-}{1 \text{ mol solute}} = 0.30 \qquad [Cl^-] = 0.30$

The highest concentration of Cl^- ions is found in solution D, 0.20 M $MgCl_2$.

The correct choice is (D).

2. Osmotic pressure, a colligative property, is lowered by the presence of particles in solution. The correct choice identifies the solution with the smallest total molarity of all ions.

The correct choice is (B).

3. The solution with the highest vapor pressure is the solution that has the lowest concentration of all ions. See solution to question (2) above.

The correct choice is (B).

4. Of the samples listed, the solution with the greatest mass is 500 mL of 0.10 M NaCl, choice (B). At 500 mL of solution, the mass of the system includes nearly 500 g H_2O plus 2.9 grams (0.05 mol) of solute. The next closest value is 400 mL of 0.030 M NH_4Cl, with nearly 400 g H_2O.

The correct choice is (B).

5. Estimate mass of solute for each solution:

(A) NH_4Cl: $$0.400\ \text{L} \times \frac{0.30\ \text{mol solute}}{1\ \text{L solution}} \times \frac{53.5\ \text{g}}{1\ \text{mol solute}} \approx 0.12 \times 54 \approx 6\ \text{g}$$

(B) NaCl: $$0.500\ \text{L} \times \frac{0.10\ \text{mol solute}}{1\ \text{L solution}} \times \frac{58.5\ \text{g}}{1\ \text{mol solute}} \approx 0.05 \times 59 \approx 3\ \text{g}$$

(C) KCl: $$0.200\ \text{L} \times \frac{0.20\ \text{mol solute}}{1\ \text{L solution}} \times \frac{74.5\ \text{g}}{1\ \text{mol solute}} \approx 0.04 \times 75 \approx 3\ \text{g}$$

(D) $MgCl_2$: $$0.100\ \text{L} \times \frac{0.20\ \text{mol solute}}{1\ \text{L solution}} \times \frac{95.3\ \text{g}}{1\ \text{mol solute}} \approx 0.02 \times 95 \approx 2\ \text{g}$$

(E) $FeCl_3$: $$0.200\ \text{L} \times \frac{0.10\ \text{mol solute}}{1\ \text{L solution}} \times \frac{162\ \text{g}}{1\ \text{mol solute}} \approx 0.02 \times 160 \approx 3\ \text{g}$$

The question appears to call for calculations. However, a satisfactory answer can be obtained by estimating values. Estimation is also a valuable timesaver when precise calculation is not required.

The correct choice is (A).

6. Cl^- ions come from both sources:

$$0.250\ \text{L} \times \frac{0.20\ \text{mol CaCl}_2}{1\ \text{L solution}} \times \frac{2\ \text{mol Cl}^-\ \text{ion}}{1\ \text{mol CaCl}_2} = 0.10\ \text{mol Cl}^-\ \text{ions}$$

$$0.250\ \text{L} \times \frac{0.40\ \text{mol KCl}}{1\ \text{L solution}} \times \frac{1\ \text{mol Cl}^-\ \text{ion}}{1\ \text{mol KCl}} = 0.10\ \text{mol Cl}^-\ \text{ions}$$

Mixing together in 0.50 liter solution

$$\frac{0.20\ \text{mol Cl}^-\ \text{ions}}{0.50\ \text{L of solution}} = 0.40\ M$$

Other answers are results of calculations when the values provided are used incorrectly.

The correct choice is (D).

7. This system illustrates solubility equilibrium established according to the equation

$$Na_2CO_{3(s)} \rightleftharpoons 2Na^+{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}$$

Statement I is correct.

Molality is defined as moles solute per kilogram solvent; molarity is defined as moles solute per liter of solution. For most aqueous solutions, the numerical value for molality is generally greater than the corresponding value for molarity. This is especially true at high concentrations where the solute may form an appreciable fraction of the volume of the solution. Statement II is not correct.

The dissolving process is represented in the equation above. Note that two moles of the cation dissolve for every one mole of anions. Statement III is correct.

The correct choice is (D).

8. The vapor pressure of the solution varies directly with the mole fraction, χ, of the volatile solvent $(23.8 \text{ mm Hg} \times 0.90 = 21.4 \text{ mm Hg})$. Exact calculation is not required since estimation allows determination of the answer.

The correct choice is (D).

9. Density is defined as mass per unit volume. When molality is known, moles of solute per kilogram of solvent is specified.

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

To obtain mol solute per kilogram of **solution**, add mass of solute present to 1.00 kg solvent as shown below.

$$\frac{6.0 \text{ mol sucrose}}{\left(6.0 \text{ mol sucrose} \times \dfrac{0.342 \text{ kg sucrose}}{1 \text{ mol sucrose}}\right) + 1 \text{ kg solvent}}$$

The denominator gives the mass of the solute + mass of the solvent (the solution). In order to calculate density, a connection to volume of solution must be known. Molarity, moles of solute per liter of solution, provides such a connection. The expression below shows how to use the known information to obtain density.

$$\frac{\text{kg solution}}{\text{mol solute}} \times \frac{\text{mol solute}}{\text{L solution}}$$

The correct choice is (B).

10. Quick mental arithmetic shows that one mole of acetic acid is mixed with five moles of water. The mole fraction of $HC_2H_3O_2$ becomes $\frac{1}{6}$, one mole of the acid to six moles total.

The correct choice is (B).

11. Molarity is defined as moles of solute per liter of solution. The number of moles of solute determined by calculation is generally measured by weighing. However, the quantity of solution is specified as a volume. Of those listed, the device for measuring volume with the greatest precision is the volumetric flask.

    The correct choice is (B).

12. For mass percent, solute (component) is compared to solution (total mixture). Thus 25 g solute compared to 125 g total in the solution gives 20%.

    The correct choice is (B).

13. If the final rinsing of a buret in a titration experiment is taken with water rather than the standard solution, the standard solution becomes slightly diluted by residual water in the buret as its initial volume reading is taken. Thus, an apparently slightly larger volume of the standard solution will have been added to the reaction mixture when the endpoint is reached. This causes the number of moles of base used to be reported too large and therefore the number of moles of acid reacting is also reported too large. The mistake does not affect the volume of solute used for the solid acid. (That volume is not used in any calculation for the assigned result.) Only statement III is correct.

    The correct choice is (C).

14. Parts per million refers to mass of solute per million units of mass of solvent. Drinking water with 0.050 ppm arsenic contains 0.050 g arsenic per 10^6 (million) grams of water. One way to respond to this question is to change each answer to the same units as given, i.e., ..?.. g arsenic per 10^6 (million) grams of water

    (A) $\dfrac{0.050\text{ mg As}}{1\text{ mL water}} \times \dfrac{1\text{ g}}{1000\text{ mg}} \times \dfrac{1\text{ mL water}}{1\text{ g water}} \times \dfrac{10^6}{\text{million}} = \dfrac{50\text{ g As}}{\text{million g water}}$

    (B) $\dfrac{0.050\text{ mg As}}{1\text{ liter water}} \times \dfrac{1\text{ g}}{1000\text{ mg}} \times \dfrac{1\text{ liter water}}{1000\text{ g water}} \times \dfrac{10^6}{\text{million}} = \dfrac{0.050\text{ g As}}{\text{million g water}}$

    (C) $\dfrac{0.050\text{ As}}{10^6\text{ L water}} \times \dfrac{1\text{ liter water}}{1000\text{ g water}} \times \dfrac{10^6}{\text{million}} = \dfrac{0.000050\text{ g As}}{\text{million g water}}$

    (D) $\dfrac{0.050\text{ mg As}}{10^6\text{ L water}} \times \dfrac{1\text{ g}}{1000\text{ mg}} \times \dfrac{1\text{ liter water}}{1000\text{ g water}} \times \dfrac{10^6}{\text{million}} = \dfrac{0.000000050\text{ g As}}{\text{million g water}}$

    (E) $\dfrac{0.050\text{ mg As}}{10^6\text{ g water}} \times \dfrac{1\text{ g}}{1000\text{ mg}} \times \dfrac{10^6}{\text{million}} = \dfrac{50\text{ g As}}{\text{million g water}}$

    The value, 0.050 mg As per liter of water, choice (B), is another way to express 0.050 ppm.

    The correct choice is (B).

15. Since the denominator of molality is kg of solvent and there is 0.1 kg (100 g) of water, you must find a temperature where approximately 0.3 moles (about 22 g) of KCl will dissolve.

    The correct choice is (A).

16. Mass percentage of the solution is given by $\frac{(100 \text{ g water})}{(100 \text{ g water} + 50 \text{ g KCl})}$ which is equivalent to 67%.

    The correct choice is (D).

17. The amount of solute dissolved is temporarily above the solubility curve, hence supersaturated.

    The correct choice is (E).

18. The quantity of solute precipitated is represented by the difference between 40 g and the solute value represented on the solubility curve at 40°C, about 2 g.

    The correct choice is (B).

19. The Tyndall effect is the glow observed along the path of a beam of light shining through a colloid. This effect is not observed in a solution because the dispersed particles are too small to affect light. Since the particles of a suspension are much larger, that type of dispersion is opaque to visible light.

    The correct choice is (A).

20. The stearate ion, $C_{17}H_{35}COO^-$, is large enough to have a charged part that is attracted to water and an uncharged part that is attracted to nonpolar molecules. Hydrophobic molecules are likely to be nonpolar molecules that form strong intermolecular attractions with each other and thus "repel" water. In the presence of the stearate ion, those molecules are attracted to stearate ions and repulsion to water decreases. This accounts for the cleaning action of ordinary soap.

    The correct choice is (E).

21. Adding water to a solution of potassium nitrate will cause the solution to become more dilute in potassium nitrate. In addition, the volume of the solution will increase. At lower concentration, the solution will have higher vapor pressure and higher freezing point (options I and II). Its mass per unit volume (density) will decrease (option III). Its properties become more like pure water.

    The correct choice is (E).

22. In this solution, the addition of NaCl to water causes density to increase, vapor pressure to decrease, freezing point to decrease, and osmotic pressure to increase. The lower vapor pressure accounts for the increase in the boiling point as the solute is added to the solution, not lower boiling point as in choice (C).

The correct choice is (C).

23. In a spontaneous, exothermic dissolving process, ΔG_{soln} is negative (spontaneous process), ΔH_{soln} is negative (exothermic process), and ΔT is positive because the energy given off causes the temperature of the system to increase. Only options I and II are correct.

The correct choice is (C).

24. Increasing the temperature while maintaining contact with excess solute causes more solute to dissolve. Both molality and density of the solution increase (options I and III). The solution remains saturated because it remains in contact with excess solute (option II).

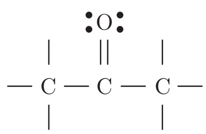
The correct choice is (E).

25. Increasing the temperature of any aqueous NaCl solution causes the vapor pressure to increase because the vapor pressure of the solvent increases (option I). The number of ion pairs in solution remains the same because in a dilute solution of an ionic solid such as NaCl, the solute is fully dissociated. The difference between the boiling point and the freezing point remains the same because the concentration of the solution remains the same. Options II and III are not correct.

The correct choice is (A).

Free Response Questions

26. **Strategy**: Recognize that propanone is a ketone, a hydrocarbon derivative with the general formula R-CO-R′.

(A) CH_3COCH_3 

(B) Propanone forms a solution with water because both are polar molecules ("like dissolves like"). Polar solutes dissolve readily in polar solvents. The greater the attractive forces between the solvent and solute molecules, the greater the solubility.

(C) It is helpful to set up a table to organize the information.

	propanone	**2-propanol**	**solution**
volume	30.0 mL	50.0 mL	80.0 mL
density	0.792 g mL^{-1}	0.785 g mL^{-1}	N/A
mass	23.8 g	39.3 g	63.1 g
moles*	0.410 mol	0.654 mol	N/A

* Calculated using molar mass. Because the solution is a mixture with no molar mass, it is not correct to calculate "moles of solution". The solution is a mixture of 0.410 mol solute and 0.654 mol solvent. The total number of moles of particles in the mixture is 1.064 mol.

(i) $\dfrac{39.3 \text{ g 2-propanol}}{63.1 \text{ g solution}} = 0.623 \times 100\% = 62.3\%$ 2-propanol by mass

(ii) $\dfrac{30.0 \text{ mL propanone}}{80.0 \text{ mL solution}} = 0.375 \times 100\% = 37.5\%$ propanone by volume

(iii) $\dfrac{0.410 \text{ mol propanone}}{1.064 \text{ mol total}} = 0.385$ mole fraction propanone

(D) The freezing point of the solution is expected to be lower than that of the pure solvent, an example of one colligative property of the solution. The presence of propanone particles in the 2-propanol interferes with the arrangement of solvent particles as they change from the disorder of a liquid into an orderly solid lattice, thus requiring more energy to be removed from the system. A lower freezing point is established.

27. Strategy: Dissolving of a solid solute in a liquid solvent requires separation of solute particles, attraction of solute particles to solvent and separation of solvent particles to provide space for the dissolving solute. As these components of the dissolving process occur, the solute becomes dispersed into the solvent to form the solution, a mixture of molecule and ion size particles.

(A) The two major energy changes related to dissolving are **lattice energy** and **hydration energy.**

- Lattice energy is the energy required to overcome attraction between solute particles in the solid phase and separate the solute into particles small enough to be dispersed in the solvent. Those particles are generally ions or molecules.
- Hydration energy is the energy released when the solute particles are attracted to the water molecules.

(B) As an ionic solid dissolves in water, entropy increases. The ionic solid is a highly ordered system. When dissolved in water, the extent of disorder (randomness) increases. Hydrated ions become randomly dispersed throughout the mixture. The entropy change, ΔS, is given by $\Delta S = S_{prod} - S_{react}$. In the dissolving process for an ionic solid, S_{prod} is generally greater than S_{react}; therefore ΔS is positive.

(C) Providing the lattice energy requires input of energy. Hydration of solute particles releases energy. The balance struck between these changes helps determine the solubility of the ionic solid. When the hydration energy is greater than the lattice energy, (that is, when the algebraic sum of these energy changes is negative), ΔH is negative and solubility tends to be greater. (See also part D below.)

(D) In order for an ionic solid to be soluble, the value for ΔG for the dissolving process must be negative. In the relationship, $\Delta G = \Delta H - T\Delta S$, ΔS is nearly always positive because the system becomes more disordered as dissolving occurs. The ΔH term is the algebraic sum of the hydration energy (exothermic, negative) and the lattice energy (endothermic, positive). When ΔH is negative and ΔS is positive as above, ΔG is negative at all values of T and the dissolving process occurs at any temperature. However, when ΔH is positive, it is the magnitude of the $T\Delta S$ term that determines whether or not ΔG is negative, that is, whether or not the dissolving process does occur. At higher temperatures, increasing entropy plays a greater role in determining solubility.

(E) The dissolving process for ammonium nitrate, NH_4NO_3, in water is endothermic.

(1) **The temperature of the mixture decreases.** In an endothermic dissolving process, heat is absorbed from the surroundings. The vessel and the system become colder; that is, temperature of the system and its container decreases.

(2) **If the amount of solute to be dissolved is doubled, the amount of decrease in temperature, ΔT, is expected to be doubled.** In the dissolving process, twice as much energy is absorbed from the surroundings in order to overcome the attractive forces between twice as many particles of solute.

28. Strategy: Preparation of any solution calls for the determination of measurable amounts of any two of the following:

- solute, most often a solid or liquid
- solvent, usually a liquid
- solution, usually a liquid

Measurable amounts could be expressed as mass or volume. The mass and volume of the resulting mixture are determined by the amounts of solute and solvent that are mixed together. Note that masses of solute and solvent must add up to give the mass of the solution. However, the volumes of the solute plus solvent do not necessarily add up to the volume of the solution formed. Thorough mixing of the solute and solvent generally produces a mixture with less volume than the sum of its components. In addition, the volume of a given mass of solid solute to be dissolved is easily affected by the degree of subdivision of that solid.

(A) Measure, precisely to two significant figures, 0.50 mol, that is, 49 grams, of H_2SO_4. A balance may be used for weighing the assigned quantity. Alternatively, to use volumetric equipment such as graduated cylinder, pipet or buret, the volume that contains the specific mass can be calculated from the specific gravity information supplied with the concentrated sulfuric acid. The assigned quantity of solute is 0.50 mol and the concentration of the solution to be 1.0 M; therefore, the volume of the solution to be prepared is 0.50 liter. Obtain a heat-resistant (borosilicate) volumetric flask with volume specified as 500 mL. Add enough distilled water so that the flask is at least half-filled. Then carefully add the measured 0.50 mole of liquid H_2SO_4 to the water. (A very noticeable exothermic reaction will occur.) Swirl gently to mix. When the mixture has cooled to room temperature, add distilled water until the meniscus is at the 500 mL mark on the neck of the flask. (Note: it is **not** correct, and actually unsafe, to add any amount of water to the measured amount of acid.)

(B) Again, the assigned amount of solute, H_2SO_4, is 0.050 mol (49 grams), obtained either by weighing or taking a measured volume. To use all of this solute, the amount of solvent needed is precisely 500 g (500 mL). The solution must be prepared in a heat-resistant vessel that holds more than 500 mL of solution because the volume of the assigned amount of H_2SO_4 is added to the 500 g (500 mL) of water.

(C) **The percent by mass of H_2SO_4 is greater in the 1.0 M solution.** The mass of H_2SO_4 used for each solution is the same. For the 1.0 M solution, the mass of water used is some amount less than 500 g (500 mL). The mass of water used for the 1.0 m solution is precisely 500 g. Therefore, the solution with the lesser amount of water has a greater percent by mass of H_2SO_4.

(D) As with any laboratory activity, use of safety goggles and protective clothing is necessary. When working with any acid, it is a general rule to always add acid to water. Concentrated H_2SO_4 is very corrosive to the skin. In addition, as it is mixed with water, much energy is evolved. To avoid boiling and spattering, sulfuric acid should always be added to water slowly and with constant mixing. Mixing should always be done in heat-resistant glassware and in a sink or other space where dilution of any spills can be carried out safely.

(E) **For this process, crystal lattice energy is greater than hydration energy.** In an endothermic dissolving process, more energy is taken on (stored) than given off (released). In this process, more energy is taken on as crystal lattice energy (bonds broken) than is given off as hydration energy (bonds formed).

Multiple Choice Questions

Questions 1-5: The set of lettered choices is a list of aqueous solutions of chloride compounds in various amounts. 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) 400 mL of 0.30 M NH_4Cl (molar mass: 53.5 g)
(B) 500 mL of 0.10 M NaCl (molar mass: 58.5 g)
(C) 200 mL of 0.20 M KCl (molar mass: 74.5 g)
(D) 100 mL of 0.20 M $MgCl_2$ (molar mass: 95.3 g)
(E) 200 mL of 0.10 M $FeCl_3$ (molar mass: 162 g)

1. contains the highest concentration of Cl^- ions

2. has the highest osmotic pressure

3. has the highest vapor pressure

4. has the greatest mass of solution

5. has the greatest mass of solute

---

6. What is the final concentration of Cl^- ion when 250 mL of 0.20 M $CaCl_2$ solution is mixed with 250 mL of 0.40 M KCl solution? (Assume additive volumes.)

   (A) 0.10 M
   (B) 0.20 M
   (C) 0.30 M
   (D) 0.40 M
   (E) 0.60 M

7. Which statement applies to a saturated aqueous solution of the highly soluble salt, sodium carbonate, Na_2CO_3, in contact with excess solid at constant temperature?

   I. The system illustrates solubility equilibrium.
   II. The molarity of the solution is equal to its molality.
   III. The rate at which anions dissolve is less than the rate at which cations dissolve.

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

8. A solution is prepared by dissolving 1.00 mol glycerol, a nonvolatile nonelectrolyte, in 9.00 mol water. The vapor pressure of water at 25°C is 23.8 mmHg. The vapor pressure of the solution in mmHg is

(A) 0.147
(B) 0.853
(C) 2.38
(D) 21.4
(E) 23.8

9. A water solution of sucrose ($C_{12}H_{22}O_{11}$, molar mass: 342) is known to be 6.0 molal. What one additional characteristic of the solution could be used to determine its density?

(A) mass
(B) molarity
(C) boiling point
(D) freezing point
(E) percent by mass

10. Which ratio gives the mole fraction of $HC_2H_3O_2$ when 60.0 g acetic acid ($HC_2H_3O_2$, molar mass: 60.0 g) is dissolved in 90.0 g water (H_2O, molar mass: 18.0 g)?

(A) $\frac{1}{5}$
(B) $\frac{1}{6}$
(C) $\frac{2}{3}$
(D) $\frac{2}{5}$
(E) $\frac{11}{1}$

11. When used to prepare a standard solution of solid acid with specified molarity, which apparatus provides the greatest precision for measuring the specified quantity of solution to be prepared?

(A) Dewar flask
(B) volumetric flask
(C) Erlenmeyer flask
(D) analytical balance
(E) centigram balance

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.

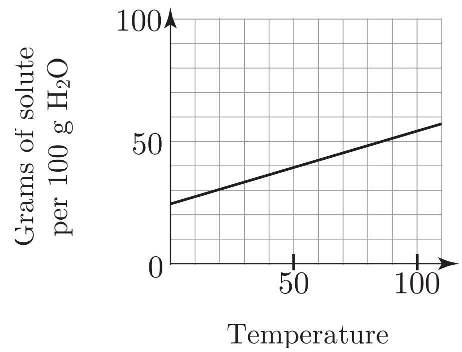
III. The reported number of moles of unknown acid used in the titration reaction is too large.

(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.

7. The sublevel for an electron is identified by the second quantum number. In every energy level above the first energy level, there is a *p*-sublevel, with the numeral “1” as the second quantum number for each electron found in the *p*-sublevel. Thus, any correct set of quantum numbers with “1” as a second quantum number (and with 2 or higher as the first quantum number) identifies a *p*-sublevel electron.

   The correct choice is (D).

8. In this situation, radius increases when electrons are gained by a sulfur atom to form the sulfide ion.: $S^0 + 2e^- \rightarrow S^{2-}$

   These two electrons are added to the $3p$ sublevel. Thus, option I is not correct but option II is. Some electrons are found in the first three energy levels for both species. Option III is a true statement.

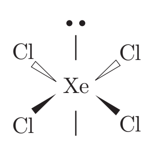
   The correct choice is (E).

Questions 9–11: As multiplicity of a bond increases (more shared pairs of electrons), bond length becomes shorter, while bond energy and bond strength become greater. H_2, F_2 and Cl_2 have single bonds. Most authorities assign O_2 a bond order between 1 and 2. Only N_2 contains a triple bond. This bond with the greatest multiplicity is the shortest bond as well as the strongest.

9.–11. The correct choices are all (B).

Questions 12–14: $XeCl_4$ and $I_3{}^-$ form the same electron pair (electron domain) geometry with expanded octets to accommodate six electron pairs. These six electron pairs are arranged in six d^2sp^3 hybrid orbitals with octahedral geometry. The six pairs of electrons in $XeCl_4$ are distributed as four shared (bonding) pairs and two unshared (lone) pairs; $I_3{}^-$ has two shared pairs and four unshared pairs. The electron domain geometry for the five pairs of IF_3 is based on five dsp^3 hybrid orbitals with trigonal pyramidal geometry for three shared pairs and two unshared pairs. The molecular geometries are interpreted only after the electron pair geometries have been ascertained. See diagrams below:

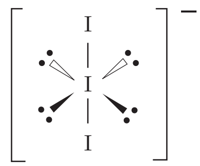
12. $XeCl_4$



   The molecular geometry is square planar with four Cl atoms bonded at equatorial positions of the octahedron.

   The correct choice is (C).

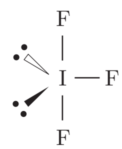
13. I_3^-



The geometry of this polyatomic ion is linear with two I atoms bonded at axial locations of the octahedron.

The correct choice is (A).

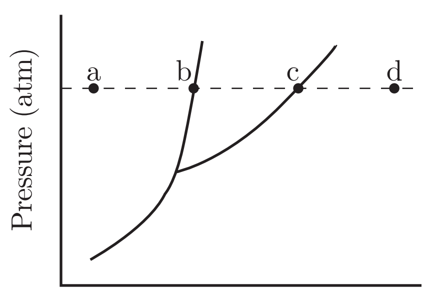
14. IF_3



The molecular geometry is T-shaped with three F atoms bonded at one equatorial and two axial locations. Note that the two unshared pairs are located in equatorial positions approximately 120° apart to minimize repulsion effects.

The correct choice is (E).

15. The phase diagram below is taken from the question book.



The answer choices refer to:

(A) change in temperature from *a* to *b*:	warming as a solid
(B) equilibrium with constant temperature at *b*:	solid to liquid phase change at the normal melting point
(C) change in temperature from *b* to *c*:	warming as a liquid
(D) equilibrium with constant temperature at *c*:	liquid to gas phase change at the normal boiling point
(E) change in temperature from *c* to *d*:	warming as a gas

Because energy is added at a constant rate and the phase change at point *c* requires the greatest amount of energy, of the five changes represented, this phase change requires the greatest amount time.

The correct choice is (D).

16. The electron distribution in SO_2 is based on sp^2 hybrid orbitals (bond angle approximately 120°), while in CO_2 that distribution is based on sp hybrid orbitals (bond angle approximately 180°). Option I is not true. Option II is true and helps explain why forces of attraction are greater between molecules of SO_2 than between molecules of CO_2. Option III is true but unrelated to deviation from ideal behavior.

The correct choice is (B).

17. Look for the highest "concentration" of water. Note that the vapor pressure of a water solution is greatest where there is the lowest concentration of dissolved particles of nonvolatile solute in the solution. The list of these systems in order of increasing vapor pressure is

First	0.2 m KNO_3	0.4 mol dissolved particles per kg water
	0.1 m $CaCl_2$	0.3 mol dissolved particles per kg water
	0.2 m $(NH_2)_2CO$, urea	0.2 mol dissolved particles per kg water
	0.1 m $C_6H_{12}O_6$, glucose	0.1 mol dissolved particles per kg water
Fifth	0.1 m C_2H_5OH	0.1 mol dissolved particles per kg water plus C_2H_5OH vapor

Note also that C_2H_5OH is a volatile solute and, at 0.1 m concentration, contributes an additional small amount to the total vapor pressure. The glucose solution (choice D) is in fourth place.

The correct choice is (D).

18. Molarity is defined as moles of solute per liter of solution. In this case, 0.100 mol (8.01 g) NH_4NO_3 is dissolved in 0.250 liter solution; thus, its concentration is 0.40 M.

The correct choice is (C).

19. The solution with the greatest number of moles of dissolved particles has the highest boiling point. The concentration of dissolved particles in the $SrBr_2$ solution, allowing for 100% dissociation of ions, is 0.3 m. This solution has the highest boiling point. The other ionic solutes specified (KBr and $MgSO_4$) also dissociate completely but give fewer ions per "molecule". Ethanol (C_2H_5OH) does not dissociate to any appreciable extent. Acetic acid (CH_3COOH), a weak acid, dissociates only slightly (less than 1%).

The correct choice is (A).

20. Perchloric acid ($HClO_4$) is a strong acid, dissolving readily in water. Trichloromethanol (CCl_3OH) is polar and dissolves slightly while tetrachloromethane (CCl_4) is nearly insoluble in water. Silver chloride (AgCl) and lead(II) chloride ($PbCl_2$) are nearly insoluble ionic solid salts.

The correct choice is (E).

21. Although most solids are more soluble in water at higher temperatures, gases are more soluble in liquids at lower temperatures where the average kinetic energy of the system including gas molecules is less. Bubbles of CO_2 can be better kept dissolved in soda if the bottle is placed in the refrigerator (lower T) with the cap on (to maintain higher P above the surface of the solution).

    The correct choice is (C).

22. The solution contains 1.0 mol CH_3COOH dissolved in 0.090 kg (5×18 g) water. The molality is given by $\frac{1}{0.090}$ as in choice (A).

    The correct choice is (A).

23. At the simplest determination, a solution that is 0.50 χ (mole fraction) in ethanol contains 1 mol ethanol - 46 grams - plus 1 mol water -18 grams - for a total of 64 grams. Thus, the solution is 72% ethanol ($46/64 \times 100$). By estimation arithmetic, the student should recognize that 32/64 is 50% (choice C), concluding that the correct value is greater than 50%. The student should also recognize that $58/64 \approx 90\%$ with the inference that the correct value is somewhere between 50% and 90%, corresponding to choice (D) at 75%.

    The correct choice is (D).

24. The empirical formula is determined by calculating the relative number (or moles) of atoms of each component element. The mass percent $\times$ 1/atomic mass = number of moles of that atom present in 100 grams of the compound. Choice (D) represents such a calculation. The other choices represent other numerical manipulations. (While this calculation is not required to choose the correct answer, it is shown below to illustrate the arithmetic needed to determine the actual empirical formula in its proper format - integers.)

    $Mn_{\frac{69.6}{55}} \quad O_{\frac{30.4}{16}}$

    $Mn_{1.27} \quad O_{1.90}$

    $Mn_{\frac{1.27}{1.27}} \quad O_{1.90}$

    $Mn_{1} \quad O_{\frac{1.5}{1.27}}$ or Mn_2O_3

    The correct choice is (D).

25. The correctly balanced half-reaction is shown below:

$$NO_3{}^- + 10H^+ + 8e^- \rightarrow NH_4{}^+ + 3H_2O$$

    Note that the coefficients of $NO_3{}^-$ and $NH_4{}^+$ are *understood* to be "1". The sum of the coefficients is: $1 + 10 + 8 + 1 + 3 = 23$.

    The correct choice is (E).

76. Overall strategy: Recognize this problem as a gas phase homogeneous equilibrium system, where the equilibrium constant is given in K_p format. Note that parts (c) and (d) present systems that start as mixtures that become equilibrium systems.

(a) $K_p = (P_{NH3})\ (P_{H2S})$

(b) $P_{NH3} + P_{H2S} = P_T = 0.660$ atm

Note that equal molar quantities of $NH_{3(g)}$ and $H_2S_{(g)}$ are produced when the solid decomposes.

Therefore,

$P_{NH3} = P_{H2S} = 0.330$ atm

$K_p = (P_{NH3})\ (P_{H2S}) = (0.330)(0.330)$

$K_p = 0.109$ atm

(c) (i) $K_p = (P_{NH3})\ (P_{H2S}) = (3\ P_{H2S})\ (P_{H2S}) = 0.109$

$3\ (P_{H2S})^2 = 0.109$

$P_{H2S} = 0.191$ atm

(ii) 0.330 atm H_2S original equilibrium

0.191 atm H_2S at new equilibrium

0.139 atm H_2S converted to NH_4HS

Use the General Gas Law to determine moles H_2S lost, hence moles NH_4HS formed

$$n_{H_2S} = \frac{P_{H_2S} \times 5.00\ \text{L}}{0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}$$

$$n_{H_2S} = \frac{0.139\ \text{atm} \times 5.00\ \text{L}}{0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}} = 0.0284\ \text{mol } NH_4HS_{(s)}$$

$n_{H_2S} =$ **+0.0284 mol NH_4HS formed**

(d) (i) $K_p = (P_{NH3})\ (P_{H2S}) = 0.109$

$(P_{NH3})\ (0.750) = 0.109$

$P_{NH3} = 0.145$ atm

(ii) If 0.250 atm H_2S lost as equilibrium was achieved, then 0.250 atm NH_3 also lost.

Original $P_{NH3} = 0.250$ atm lost + 0.145 atm remaining at equilibrium

Original $P_{NH3} = 0.395$ atm

77. Overall strategy: This is an illustration of a set of experiments that are based on the differential rate laws. The following data were obtained from a study of the kinetics of the reaction below at 298 K.

$$5Br^- + BrO_3{}^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

	initial concentration mol L^{-1}			rate of formation of Br_2 moles sec^{-1}
Trial	$[Br^-]$	$[BrO_3{}^-]$	$[H^+]$	Br_2
I.	1.0×10^{-3}	5.0×10^{-3}	$10. \times 10^{-3}$	2.5×10^{-4}
II.	2.0	5.0	10.	5.0
III.	1.0	10.	10.	2.5
IV.	1.0	5.0	20.	10.
V.	2.0	10.	20.	?

(a)
- for order of Br^-, compare trials I & II
- for order of $BrO_3{}^-$, compare trials I & III
- for order of H^+, compare trials I & IV and III & IV

$\text{Rate} = k\,[Br^-]^1[BrO_3{}^-]^0[H^+]^2$ overall third order

$[BrO_3{}^-]^0 = 1$; therefore not needed in Rate Law

$\text{Rate} = k\,[Br^-]^1[H^+]^2$

(b) Choose trial III for easiest arithmetic

$$\text{Rate} = \text{k}\ [Br^-]^1[H^+]^2$$

$$2.5 \times 10^{-4} = k\ (1.0 \times 10^{-3})^1\ (10. \times 10^{-3})^2$$

$$k = 2.5 \times 10^3\ L^3\ mol^{-2}\ sec^{-1}$$

(c) What is the predicted initial rate of formation of bromine in trial V?

$\text{Rate} = 2.5 \times 10^3\ L^3\ mol^{-2}\ sec^{-1}\ [Br^-]^1[BrO_3{}^-]^0[H^+]^2$

$\text{Rate} = 2.5 \times 10^3\ L^3\ mol^{-2}\ sec^{-1}\ (2.0 \times 10^{-3})^1\ (10 \times 10^{-3})^0\ (20 \times 10^{-3})^2$

$\text{Rate} = 2.0 \times 10^{-3}\ mol\ sec^{-1}$

(d) (i) Br^- limits extent of reaction, hence is consumed.

Loss of $BrO_3{}^-$ is $\dfrac{-1\ mol\ BrO_3{}^-}{5\ mol\ Br^-}$

Loss of H^+ is $\dfrac{-6\ mol\ H^+}{5\ mol\ Br^-}$

$BrO_3{}^-$ remains at highest concentration

(ii) $[BrO_3{}^-]$ 10.0×10^{-3} available

-0.4×10^{-3} lost

9.6×10^{-3} remain

$2.0 \times 10^{-3}\ M\ Br^-$ consumed $\times \dfrac{-1\ mol\ BrO_3{}^-}{5\ mol\ Br^-}$

$0.4 \times 10^{-3}\ M\ BrO_3{}^-$ lost; $9.6 \times 10^{-3} M\ BrO_3{}^-$ remains

78. Overall strategy: This problem calls for application of principles of stoichiometry and the General Gas Law.

(a) (i) Use the General Gas Law to determine the number of moles of N_2.

$$n = \frac{PV}{RT}$$

$$= \frac{\frac{746}{760}\text{ atm} \times 0.0378\text{ L}}{0.0821\text{ L atm mol}^{-1}\text{ K}^{-1} \times 296.8\text{ K}}$$

$$= 0.001478\text{ mol N}_2$$

Convert this to mass of nitrogen.

$$(0.001478)\text{mol N}_2 \times \frac{28.0\text{ g N}_2}{1\text{mol N}_2} = 0.04141\text{ g N}_2$$

Compare to the original mass of the compound to determine the percent by mass.

$$\frac{0.04141\text{ g N}_2}{0.4788\text{ g compound}} = \mathbf{8.65\%\ nitrogen}$$

(ii) This amount of carbon dioxide contains 9.58 mg C, equivalent to 74.0% by mass of the compound. This amount of water contains 0.9682 mg H, equivalent to 7.47% by mass of the compound.

$$35.14\text{ mg carbon dioxide} \times \frac{12\text{ g C}}{44\text{ g CO}_2} = 9.58\text{ mg C}$$

$$\frac{9.58\text{ mg C}}{12.96\text{ mg of the compound}} = \mathbf{74.0\%\ carbon}$$

$$8.638\text{ mg water} \times \frac{2\text{ g H}}{18\text{ g H}_2\text{O}} = 0.9682\text{ g H}$$

$$\frac{0.9682\text{ g H}}{12.96\text{ mg of the compound}} = \mathbf{7.47\%\ hydrogen}$$

(iii) To find the remaining percentage by mass oxygen, subtract the percentages of nitrogen (from part a) and carbon and hydrogen (from part b) from 100%.

$$\%\text{O} = 100 - \%\text{N} - \%\text{C} - \%\text{H}$$

(b) (i) Assume a 100 g sample so that each percentage becomes a mass in grams. Convert each to moles

$$25.4 \text{ g C} \times \frac{1 \text{ mol C}}{12 \text{ g C}} = 2.11 \text{ mol C}$$
$$3.2 \text{ g H} \times \frac{1 \text{ mol H}}{1 \text{ g H}} = 3.17 \text{ mol H}$$

$$37.5 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.5 \text{ g Cl}} = 1.06 \text{ mol Cl}$$

$$33.9 \text{ g O} \times \frac{1 \text{ mol O}}{16 \text{ g O}} = 2.12 \text{ mol O}$$

to determine moles of atoms of each element.
Divide each by the smallest number of moles (Cl in this problem) to find the empirical formula (simplest whole number ratio of atoms):

$$C_{\frac{2.11}{1.06}} \quad H_{\frac{3.17}{1.06}} \quad Cl_{\frac{1.06}{1.06}} \quad O_{\frac{2.11}{1.06}} \quad = \quad C_2H_3Cl_1O_2$$

(ii) In order to determine the molecular formula, the molar mass of the compound is needed. Dividing molar mass by the mass of the empirical formula gives the number of times to repeat the empirical formula to determine the molecular formula.

79. Overall Strategy: The responses to question 79 (question 4 on the exam) are often called net ionic equations, even though they are not truly equations because they are not balanced to maintain conservation of atoms and charge. It is helpful to approach these net ionic equations in a systematic way. One suggested order of analysis is based on the categories of reactions below:

- precipitation (requires knowing solubility rules)
- acid/base (requires knowing acid-base patterns)
- combustion (reaction with oxygen)
- redox (reaction containing an elemental form or a common oxidizing or reducing agent)
- complexation (requires knowing some common ligands)

See also information at question 79 for the other Sample Examinations.

(a) $OH^- + Al(OH)_3 \rightarrow Al(OH)_4{}^-$

or

$OH^- + Al(H_2O)_3(OH)_3 \rightarrow Al(H_2O)_2(OH)_4{}^- + H_2O$

Aluminum hydroxide is amphiprotic; that is, that it can act either as an acid or a base, depending on the context. In this case, in the presence of excess OH^-, hydrated $Al(OH)_3$ $\big(Al(H_2O)_3(OH)_3\big)$ acts as an acid, donating a proton to the base, hydroxide, OH^-, to yield $Al(H_2O)_2(OH)_4{}^-$.

(b) $H^+ + Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+} + H_2O$

Permanganate is an excellent oxidizing agent. With the oxidation number of Mn at +7, MnO_4^- can only be reduced. In acid solution, it is reduced to Mn^{2+}. Since the permanganate is reduced, the iron(II) must be oxidized to iron(III). This half-reaction that can be found on the Standard Reduction Potential Table. The presence of the acid proton (or hydronium) on the reactant side means that water must be listed on the product side.

(c) $C_{10}H_{21}OH + O_2 \rightarrow CO_2 + H_2O$

You should learn the name and formula of each alkane through ten carbons (methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, and decane). Note that knowing "decade" means ten years is a good memory prompt for the alkane "decane". The formula of the alcohol of each alkane merely requires the replacement of one hydrogen by an alcohol group (-OH). Even if you did not know the formula for the alcohol, you could earn partial credit for "$CO_2 + H_2O$".

Combustion (burning or oxidation) of a hydrocarbon or alcohol in excess oxygen (or air) always produces water and carbon dioxide as combustion products. (In limited oxygen, the products could be carbon monoxide or even uncombined carbon.)

(d) $H^+(\text{or } H_3O^+) + SO_4^{2-} + Sr^{2+} + OH^- \rightarrow SrSO_4 + H_2O$

This is an example of a strong acid - strong base reaction that creates water as a product. It is also a precipitation reaction because the other double replacement product, strontium sulfate, is insoluble. The reaction of sulfuric acid with barium hydroxide is one of the common strong acid-strong base reactions that also gives a precipitate.

(e) $Ag^+ + Cr_2O_7^{2-} \rightarrow Ag_2Cr_2O_7$

Most salts containing the Ag^+ cation, including $Ag_2Cr_2O_7$, are insoluble. This substance is a red precipitate.

(f) $Ca + N_2 \rightarrow Ca_3N_2$

This is a combustion-like reaction. A different way to think about this is to consider it as a redox reaction since it contains elemental forms as reactants. The metal calcium is oxidized to its cation. The non-metal nitrogen is reduced to its anion, nitride.

(g) $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$

The reaction of a weak acid with a strong base results in the formation of water and the conjugate base of the weak acid, according to the proton transfer principle of the Bronsted-Lowry acid-base theory.

(h) $Sn^{2+} + Co^{3+} \rightarrow Co^{2+} + Sn^{4+}$

Sn^{2+} is a commonly used reducing agent. The presence of the same anion (nitrate), often a spectator ion, is another tip that a redox reaction will occur between the two cations in solution. Tin(II) is oxidized to tin(IV) while cobalt(III) is reduced to cobalt(II).

80. Overall strategy: Recognize this problem as a simple dehydration laboratory procedure. You will need to apply principles of stoichiometry and address effects of errors in procedure.

(a) The data table should include:

- mass of crucible + lid
- mass of crucible + lid + Epsom salt
- mass of crucible + lid + Epsom salt after first heating
- mass of crucible + lid + Epsom salt after second heating
- mass of crucible + lid + Epsom salt for as many more heatings as are needed to achieve constant weight.

(b) When the mass of the sample stops changing significantly, it is assumed that all water has been driven off.

(c) Losing some of the salt means a greater change in mass. This loss of mass will be interpreted as water loss from the hydrated salt. The reported degree of hydration will be overstated.

(d) Any water left in the crucible will be driven off during heating. This extra change in mass will be interpreted as if the water loss came from the salt, thus leading to apparent increase (overstatement) of the degree of hydration.

81. Overall strategy: This problem calls for the application of several definitions and principles related to solution chemistry. Be sure to refer to the list of *Equations and Constants* to verify formulas, if you are uncertain.

(a) (i) Molality compares the number of moles of solute (NaCl) to the number of kilograms of solvent (H_2O). Since the mass percentage indicates 10 g NaCl for every 90 g H_2O, simply convert mass of NaCl (58.5 g/mol) to moles and grams of H_2O to kilograms (1000 g/kilogram).

(ii) According to the list of *Equations and Constants*, “molarity = moles solute per liter of solution”. Since the denominator of the molarity definition includes volume of the solution, either the volume of the solution OR the density (mass per unit volume) and mass must be known.

(iii) The appropriate equation, as found in the list of *Equations and Constants*, is $\Delta T_f = i\ k_f m$. Since NaCl dissociates completely into two moles of ions per mole of compound, $i = 2$. The molal freezing point depression constant, k_f, for water can be obtained from the list of *Equations and Constants*. See part (a) (i) above for a discussion of molality. Once the change in freezing point is calculated, it must be subtracted from the freezing point of the pure solvent.

(iv) Mole fraction, χ, compares the moles of solute to the total number of moles of solute and solvent (moles of solute + moles of solvent). Use molar mass for each substance to convert the mass to moles.

(b) Neither mass nor number of moles is affected by temperature but the volume of a solution does change with temperature. Of the four descriptions of concentration under consideration, only the molarity definition includes a volume term. Therefore, only molarity is affected by a change in temperature.

82. Overall strategy: In this problem, you will need to apply principles from the General Gas Law and the Kinetic Molecular Theory.

(a) Since CO molecules are lighter, they travel faster than NO molecules. Both gases have the same average kinetic energy since both are at the same temperature.

(b) According to Graham's Law as found in the list of *Equations and Constants*, the velocities will vary according to the square root of the inverse of their molar masses.

$$\frac{R_1}{R_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

$$\frac{R_1}{R_2} = \frac{\sqrt{30}}{\sqrt{28}}$$

$$R_1 = \frac{\sqrt{30}}{\sqrt{28}} R_2$$

The average speed of CO (R_1) is slightly greater than the average speed of NO (R_2).

(c) 

Since NO has an odd number of electrons (11), its Lewis structure does not illustrate the Rule of 8. (A truly acceptable Lewis structure cannot be drawn.)

(d) Both NO and CO contribute to air pollution. Both are non-metal oxides and easily oxidized to NO_2 and CO_2 in atmospheric oxygen. These more familiar acid anhydrides form acids that can reach the earth's surface as acid rain.

83. Overall Strategy: Although both elements are found in the same row of the Periodic Table their properties are quite different. Scandium is a transition metal and selenium is a non-metal. In general, metals form ionic compounds bonding as cations with non-metals as anions. Some metals also form metallic bonds with other metal atoms. Pure metals tend to be dense and good conductors of heat and electricity. They have shiny luster and are ductile (can be drawn into a wire), malleable (can be pounded into a foil) and sectile (can be cut into pieces). In contrast, non-metals form molecules with covalent bonds to other non-metals. These compounds are soft or brittle non-conductors. Most nonmetals form anions in ionic bonds with cations of metals. They are less dense than metals, are not lustrous, and tend to be brittle.

(a) Compared to scandium, selenium has a greater Z (more protons). Its cloud of electrons including the valence electrons in the fourth energy level is attracted closer to the nucleus than the electron cloud in scandium. Hence, selenium has a smaller atomic radius.

(b) Scandium loses its three valence electrons ($4s^2 3d^1$) to form a 3+ cation. Selenium can gain two electrons to become an anion (2−), isoelectronic with krypton. Selenium can also have its electrons attracted away by more electronegative atoms to forming covalent bonds as in the polyatomic ion, selenate, $SeO_4{}^{2-}$, where Se has an oxidation number of +6. Note that selenic acid, H_2SeO_4, is analogous to sulfuric acid.

(c) Elemental scandium exhibits typical metallic bonding with three valence electrons available to allow for electrical conductivity. Selenium (like sulfur) can form different covalently bonded configurations known as allotropes. Red selenium is Se_8, formed in rings as with sulfur, S_8. Grey selenium resembles a metalloid and is a shiny grey. With no metallic bonding electrons available, it is a poor conductor of electricity.

(d) Excess pure oxygen will oxidize the metal scandium to +3 and form the ionic solid oxide, Sc_2O_3. As a non-metal, selenium forms covalent bonds with oxygen atoms to produce the molecular substance, SeO_2. This compound is analgous to SO_2.

7. All of these sets of quantum numbers apply to an electron in the *p*-sublevel EXCEPT

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

   (B) 3, 1, 0, $+\frac{1}{2}$

   (C) 3, 1, 0, $-\frac{1}{2}$

   (D) 2, 0, 0, $+\frac{1}{2}$

   (E) 2, 1, 0, $+\frac{1}{2}$

8. Which is a correct comparison of a sulfide ion to a sulfur atom?

   I. The radius of the sulfur atom is greater.

   II. The sulfide ion contains more electrons.

   III. The number of energy levels occupied by electrons is the same.

   (A) I only

   (B) II only

   (C) I and II only

   (D) I and III only

   (E) II and III only

Questions 9-11: The set of lettered choices below is a list of molecular formulas for certain gases. Select the one lettered choice that best fits each numbered description of the bonds within the molecules of the gas.

(A) H_2

(B) N_2

(C) O_2

(D) F_2

(E) Cl_2

9. contains bond with greatest multiplicity

10. has the strongest bond

11. has the shortest bond length

Questions 12-14: The set of lettered choices below is a list of molecular geometries. For each numbered species, select the one lettered choice that describes its molecular geometry.

(A) linear

(B) seesaw

(C) square planar

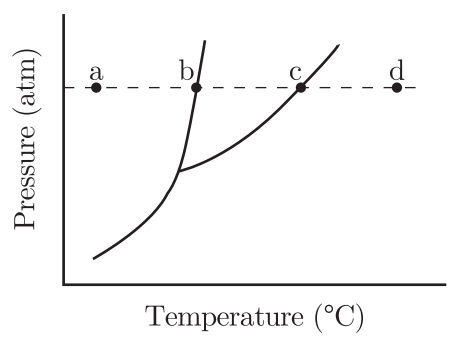
(D) square pyramidal

(E) T-shaped

12. $XeCl_4$

13. I_3^-

14. IF_3



15. The dashed line, *ad*, in the phase diagram above represents properties of a closed system as energy is added to that system at a constant rate. The properties are observed at points *a*, *b*, *c*, and *d*. Which is associated with the longest time period?

(A) change in temperature from *a* to *b*

(B) equilibrium with constant temperature at *b*

(C) change in temperature from *b* to *c*

(D) equilibrium with constant temperature at *c*

(E) change in temperature from *c* to *d*

16. Which gives a reason why, compared to CO_2, SO_2 exhibits greater deviation from ideal gas behavior?

I. The O-S-O bond angle is greater than the O-C-O bond angle.
II. A molecule of SO_2 contains more electrons than a molecule of CO_2.
III. The bond order of the S-O bond is less than the bond order of the C-O bond.

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

17. When these five water solution systems are listed in order of increasing vapor pressure, which position is occupied by 0.1 m $C_6H_{12}O_6$, glucose? (Assume ideal behavior.)

0.2 m KNO_3
0.2 m $(NH_2)_2CO$, urea
0.1 m $CaCl_2$
0.1 m C_2H_5OH
0.1 m $C_6H_{12}O_6$, glucose

(A) first
(B) second
(C) third
(D) fourth
(E) fifth

18. A solution is prepared by dissolving 8.01 g of ammonium nitrate, NH_4NO_3 (molar mass: 80.1 g), in enough water to yield 250.0 mL of solution. What is the molarity of ammonium nitrate in this solution?

(A) 32.0 M
(B) 4.00 M
(C) 0.400 M
(D) 0.100 M
(E) 0.0400 M

19. Which aqueous solution has the highest boiling point?

(A) 0.1 m $SrBr_2$

(B) 0.1 m KBr

(C) 0.1 m $MgSO_4$

(D) 0.1 m CH_3COOH

(E) 0.1 m C_2H_5OH

20. Which of these chlorine-containing compounds is most soluble in water?

(A) AgCl

(B) CCl_3OH

(C) CCl_4

(D) $PbCl_2$

(E) $HClO_4$

21. Which conditions of pressure and temperature favor greatest solubility of a gas into a liquid?

	P	**T**
(A)	low	low
(B)	low	high
(C)	high	low
(D)	high	high
(E)	moderate	moderate

22. A solution is prepared by dissolving 1.0 mol of acetic acid, CH_3COOH (molar mass: 60.0 g), in 5.0 mol water (molar mass: 18 g). Which expression gives the molality of this solution.

(A) $\dfrac{1}{0.090}$

(B) $\dfrac{1}{5}$

(C) $\dfrac{1}{6}$

(D) $\dfrac{60}{5 \times 18}$

(E) $\dfrac{60}{0.090}$

23. Consider a solution that is 0.50 X (mole fraction) of ethanol (molar mass: 46 g) in water (molar mass: 18 g). Which value gives the best approximation for percent by mass ethanol in that solution?

(A) 10%
(B) 25%
(C) 50%
(D) 75%
(E) 90%

24. The mass percent of one oxide of manganese is determined to be 69.6% Mn and 30.4% O. Which expression is the best representation of the empirical formula of this compound?

(A) $Mn_{\frac{69.6}{6.02}}$ $O_{\frac{30.4}{6.02}}$
(B) $Mn_{\frac{69.6}{30.4}}$ $O_{\frac{30.4}{30.4}}$
(C) $Mn_{\frac{69.6}{30.4}}$ $O_{\frac{30.4}{69.6}}$
(D) $Mn_{\frac{69.6}{55.0}}$ $O_{\frac{30.4}{16.0}}$
(E) $Mn_{\frac{55.0}{69.6}}$ $O_{\frac{16.0}{30.4}}$

25. When zinc reacts with nitric acid, one product is ammonium nitrate. When the corresponding half-reaction as shown below is balanced using the lowest integers, what is the sum of the coefficients?

$$..?..\ NO_3^- + ..?..\ H^+ + ..?..\ e^- \rightarrow ..?..\ NH_4^+ + ..?..\ H_2O$$

(A) 13
(B) 15
(C) 19
(D) 21
(E) 23

26. Consider a mixture of gases that contains 0.10 mol of $N_2O_{5(g)}$ and 0.10 mol of $NO_{2(g)}$ at STP. Which gives a correct description of a quantity of material present?

I. The number of atoms is greater than 5×10^{23}.
II. The number of molecules is greater than 1×10^{23}.
III. The volume of the sample is greater than 2.24 liters.

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

Section II

Section II - Free Response Total Time – 90 Minutes
(Multiple-Choice Questions are found in Section I.)

Part A: Question 76
and
Question 77 or Question 78
Time: 40 minutes

Access to calculators, Periodic Table, lists of standard reduction potentials, and *Equations and Constants*

(2004 Examination directions) Clearly show the method used and the steps involved in arriving at your answers. It is to your advantage to do this, because you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures. Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do not write your answers on the green insert.

Answer question 76 below. The Section II score weighting for this question is 20 percent.

76. Ammonium hydrogen sulfide is a white crystalline solid that decomposes according to the equation

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

In one experiment, solid NH_4HS was placed in a 5.0 L rigid container at 298 K. At equilibrium, the total pressure was 0.660 atm with the gas phase in contact with excess solid.

(a) Write the mass action expression, K_p, for this equilibrium system.

(b) Calculate the numerical value for K_p at 298 K.

(c) Equilibrium in this system was disturbed by the addition of $NH_{3(g)}$. A new equilibrium including the solid phase was established in which the pressure of $NH_{3(g)}$ was equal to three times the pressure of $H_2S_{(g)}$: $P_{NH3} = 3\ P_{H2S}$

(i) Calculate the partial pressure of H_2S at this new equilibrium.

(ii) Calculate the change in moles of $NH_4HS_{(s)}$ present in the system; include the correct sign for this change.

(d) In a different experiment in a different vessel at the same temperature, $NH_{3(g)}$ and $H_2S_{(g)}$ were mixed At the time of mixing, the partial pressure of H_2S was 1.00 atm. The initial partial pressure of $NH_{3(g)}$ was unknown. After equilibrium was established, the partial pressure of H_2S was 0.75 atm.

(i) Calculate the partial pressure of NH_3 at equilibrium.

(ii) Calculate the original pressure of NH_3 at the time of mixing.

Answer either question 77 or question 78 below.

(2004 examination directions) Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded.

The Section II score weighting for the question that you choose is 20 percent.

77. The following data were obtained from a study of the kinetics of the reaction below at 298 K.

$$5Br^- + BrO_3{}^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

	initial concentration mol L^{-1}			**rate of formation moles sec^{-1}**
Trial	**$[Br^-]$**	**$[BrO_3{}^-]$**	**$[H^+]$**	**Br_2**
I.	1.0×10^{-3}	5.0×10^{-3}	$10. \times 10^{-3}$	2.5×10^{-4}
II.	2.0	5.0	10.	5.0
III.	1.0	10.	10.	2.5
IV.	1.0	5.0	20.	10.
V.	2.0	10.	20.	?

(a) Write the rate law for this reaction. What is the overall order for this reaction?

(b) Calculate the rate constant, k, for this reaction. Specify units.

(c) What is the predicted initial rate of formation of bromine in trial V?

(d) When trial III has reached completion, the concentration of one of the dissolved species is greater than either of the other two dissolved species.

(i) Which of the dissolved species has the highest concentration? Explain your choice.

(ii) Calculate that concentration.

78. The following problems concern quantitative analysis of two chemical compounds.

(a) A compound known to contain only the elements carbon, hydrogen, nitrogen, and oxygen was analyzed in the laboratory.

(i) A sample of the compound with mass 0.4788 g was sent through a series of tests that converted all combined nitrogen into nitrogen gas. The nitrogen gas was collected by water displacement and yielded a volume of 37.80 mL, measured at 23.8°C and 746.0 mmHg. According to a chemical handbook, at this temperature, the vapor pressure of water is 22.1 mmHg. Using the results of this experiment, calculate the mass percent of nitrogen in the compound.

(ii) In a separate experiment, 12.96 mg of the compound was burned in a pure oxygen atmosphere. Products collected were 35.14 mg carbon dioxide and 8.638 mg water. Using the results of this experiment, calculate the mass percent of carbon and hydrogen in the compound.

(iii) Explain how to use data from both experiments to calculate the mass percent of oxygen in the compound.

(b) In a separate experiment, a different compound is shown to consist of 25.4% by mass carbon, 3.20% by mass hydrogen, 37.5% by mass chlorine, and 33.9% by mass oxygen.

(i) Determine the empirical formula of the compound.

(ii) Identify additional information about the compound that is needed in order to determine the molecular formula.

Part B: Questions 79, 80, 81 and
Question 82 or Question 83
Time: 50 minutes

Access to Periodic Table, lists of standard reduction potentials
and *Equations and Constants*
No access to calculators

Answer question 79 below: The Section II score weighting for this question is 15 percent.

79. (2004 Examination directions) 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 concentrated sodium hydroxide is poured onto solid aluminum hydroxide.

(b) Acidified solutions of iron(II) sulfate and potassium permanganate are mixed.

(c) A sample of 2-decanol is burned in excess oxygen.

(d) Solutions of dilute sulfuric acid and strontium hydroxide are mixed.

(e) Solutions of silver nitrate and sodium dichromate are mixed.

(f) A piece of calcium is heated in an atmosphere of pure nitrogen.

(g) A small quantity of dilute potassium hydroxide solution is poured into dilute nitrous acid solution.

(h) Solutions of tin(II) nitrate and cobalt(III) nitrate are mixed.

(2004 Examination directions) Your responses to the rest of the questions in this part of the examination will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

(2004 examination directions) **Answer both Question 80 and Question 81 below.** Both questions will be graded.

The Section II score weighting for these questions is 30 percent (15 percent each).

80. In order to determine the degree of hydration of Epsom salts, a hydrated form of magnesium sulfate, a student performs several laboratory tests. The student weighs a clean, dry crucible and lid. The student then adds several grams of Epsom salts to the crucible and reweighs it. The crucible and salt sample are heated over a Bunsen burner flame for five minutes; the crucible is allowed to cool, then reweighed. The crucible is then returned to the Bunsen burner flame for an additional five minutes of heating. It is allowed to cool, then is reweighed.

    (a) Prepare a data table to specify the measurements that should be taken during this procedure.

    (b) How can the student tell when this lab procedure is completed? Explain.

    (c) If the crucible is initially overheated so that some of the salt appears as a white wisp drifting away from the crucible, what effect will this have on the data recorded and on the final determination of degree of hydration? Explain.

    (d) If the empty crucible selected initially is clean but not dry, what effect will this have on the final determination of degree of hydration? Explain.

81. Consider an aqueous solution that is 10% NaCl by mass.

    (a) Identify the additional facts about the solution that are needed (can be calculated or must be determined) in order to:

        (i) calculate the molality, m, of the NaCl in the solution.

        (ii) calculate the molarity, M, of the solution.

        (iii) calculate the mole fraction, χ, of water in the solution.

        (iv) determine the freezing point of the solution at 1 atm. Assume complete dissociation of the solute.

    (b) The original solution of NaCl is heated from 20°C to 30°C at constant pressure. Which of the four measures of concentration is affected? Explain.

        - molarity
        - molality
        - mass percent
        - mole fraction

(2004 examination directions) **Answer either question 82 or question 83 below.** Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question that you choose is 15 percent.

82. Carbon monoxide and nitrogen monoxide are both gases that are found in small quantities in Earth's atmosphere.

    (a) Which gas has molecules with the greater root-mean-square speed at 25°C? Explain.

    (b) What is the ratio of the rates of effusion of CO to NO? Show a set-up for your calculation. A calculated numerical answer is not required.

    (c) Draw a reasonable Lewis structure for each molecule. Which structure does not illustrate the usual principles for construction of Lewis structures? Explain.

    (d) Both of these gases causes some pollution of the air due to burning fossil fuels in the internal combustion engines of automobiles? Explain.

83. Although the elements scandium and selenium are both found in the Period 4 (fourth row) of the Periodic Table, the physical and chemical characteristics of these two elements are quite different. Explain the following differences in properties of the elements scandium and selenium in terms of atomic structure and/or bonding.

    (a) The atomic radius of Sc is 160 *pm* while that of Se is 121 *pm*.

    (b) Scandium forms only one oxidation state but selenium has several, ranging from -2 to $+6$.

    (c) Scandium is a good conductor of electricity. Selenium is a poor conductor of electricity.

    (d) The reaction product of scandium with pure oxygen is Sc_2O_3 while selenium reacts with pure oxygen to form SeO_2.