

## CHEMISTRY

## SECTION I

Time — 1 hour and 30 minutes

NO CALCULATORS MAY BE USED WITH SECTION I.

Note: For all questions, assume that the temperature is 298 K, the pressure is 1.00 atmosphere, and solutions are aqueous unless otherwise specified.

Throughout the test the following symbols have the definitions specified unless otherwise noted.

|                          |                                 |
|--------------------------|---------------------------------|
| $T$ = temperature        | $M$ = molar                     |
| $P$ = pressure           | $m$ = molal                     |
| $V$ = volume             | L, mL = liter(s), milliliter(s) |
| $S$ = entropy            | g = gram(s)                     |
| $H$ = enthalpy           | nm = nanometer(s)               |
| $G$ = free energy        | atm = atmosphere(s)             |
| $R$ = molar gas constant | J, kJ = joule(s), kilojoule(s)  |
| $n$ = number of moles    | V = volt(s)                     |
|                          | mol = mole(s)                   |

## Part A

Directions: Each set of lettered choices below refers to the numbered statements immediately following it. Select the one lettered choice that best fits each statement and then fill in the corresponding oval on the answer sheet. A choice may be used once, more than once, or not at all in each set.

Questions 1-4 refer to the following types of energy.

- (A) Activation energy
  - (B) Free energy
  - (C) Ionization energy
  - (D) Kinetic energy
  - (E) Lattice energy
1. The energy required to convert a ground-state atom in the gas phase to a gaseous positive ion
  2. The energy change that occurs in the conversion of an ionic solid to widely separated gaseous ions
  3. The energy in a chemical or physical change that is available to do useful work
  4. The energy required to form the transition state in a chemical reaction

Questions 5-8 refer to atoms for which the occupied atomic orbitals are shown below.

- (A)  $1s$  \_\_\_\_\_  $2s$   $\uparrow$   
(B)  $1s$   $\uparrow\downarrow$   $2s$   $\uparrow\downarrow$   
(C)  $1s$   $\uparrow\downarrow$   $2s$   $\uparrow\downarrow$   $2p$   $\uparrow$  \_\_\_\_\_  $\uparrow$  \_\_\_\_\_  
(D)  $1s$   $\uparrow\downarrow$   $2s$   $\uparrow\downarrow$   $2p$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$   
(E)  $[\text{Ar}] 4s$   $\uparrow\downarrow$   $3d$   $\uparrow\downarrow$  \_\_\_\_\_  $\uparrow$  \_\_\_\_\_  $\uparrow$  \_\_\_\_\_  $\uparrow$  \_\_\_\_\_

5. Represents an atom that is chemically unreactive  
6. Represents an atom in an excited state  
7. Represents an atom that has four valence electrons  
8. Represents an atom of a transition metal
- 

Questions 9-12 refer to aqueous solutions containing 1:1 mole ratios of the following pairs of substances. Assume all concentrations are 1 *M*.

- (A)  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$   
(B)  $\text{H}_3\text{PO}_4$  and  $\text{NaH}_2\text{PO}_4$   
(C)  $\text{HCl}$  and  $\text{NaCl}$   
(D)  $\text{NaOH}$  and  $\text{NH}_3$   
(E)  $\text{NH}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$  (acetic acid)
9. The solution with the lowest pH  
10. The most nearly neutral solution  
11. A buffer at a  $\text{pH} > 8$   
12. A buffer at a  $\text{pH} < 6$

Questions 13-16 refer to the following descriptions of bonding in different types of solids.

- (A) Lattice of positive and negative ions held together by electrostatic forces
- (B) Closely packed lattice with delocalized electrons throughout
- (C) Strong single covalent bonds with weak intermolecular forces
- (D) Strong multiple covalent bonds (including  $\pi$ -bonds) with weak intermolecular forces
- (E) Macromolecules held together with strong polar bonds

13. Cesium chloride,  $\text{CsCl}(s)$

14. Gold,  $\text{Au}(s)$

15. Carbon dioxide,  $\text{CO}_2(s)$

16. Methane,  $\text{CH}_4(s)$

Questions 17-18 refer to the following elements.

- (A) Lithium
- (B) Nickel
- (C) Bromine
- (D) Uranium
- (E) Fluorine

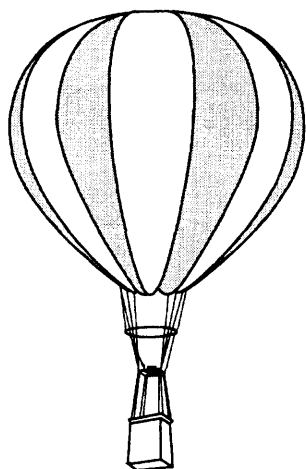
17. Is a gas in its standard state at 298 K

18. Reacts with water to form a strong base

Part B

**Directions:** Each of the questions or incomplete statements below is followed by five suggested answers or completions. Select the one that is best in each case and then fill in the corresponding oval on the answer sheet.

19. Which of the following best describes the role of the spark from the spark plug in an automobile engine?
- (A) The spark decreases the energy of activation for the slow step.
  - (B) The spark increases the concentration of the volatile reactant.
  - (C) The spark supplies some of the energy of activation for the combustion reaction.
  - (D) The spark provides a more favorable activated complex for the combustion reaction.
  - (E) The spark provides the heat of vaporization for the volatile hydrocarbon.
20. What mass of Au is produced when 0.0500 mol of  $\text{Au}_2\text{S}_3$  is reduced completely with excess  $\text{H}_2$  ?
- (A) 9.85 g
  - (B) 19.7 g
  - (C) 24.5 g
  - (D) 39.4 g
  - (E) 48.9 g
21. When a solution of sodium chloride is vaporized in a flame, the color of the flame is
- (A) blue
  - (B) yellow
  - (C) green
  - (D) violet
  - (E) white
22. Of the following reactions, which involves the largest decrease in entropy?
- (A)  $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
  - (B)  $2 \text{CO}(g) + \text{O}_2(g) \rightarrow 2 \text{CO}_2(g)$
  - (C)  $\text{Pb}(\text{NO}_3)_2(s) + 2 \text{KI}(s) \rightarrow \text{PbI}_2(s) + 2 \text{KNO}_3(s)$
  - (D)  $\text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \rightarrow 3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(g)$
  - (E)  $4 \text{La}(s) + 3 \text{O}_2(g) \rightarrow 2 \text{La}_2\text{O}_3(s)$

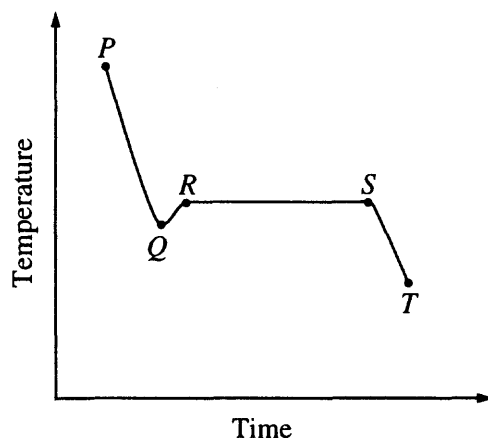


23. A hot-air balloon, shown above, rises. Which of the following is the best explanation for this observation?

- (A) The pressure on the walls of the balloon increases with increasing temperature.
- (B) The difference in temperature between the air inside and outside the balloon produces convection currents.
- (C) The cooler air outside the balloon pushes in on the walls of the balloon.
- (D) The rate of diffusion of cooler air is less than that of warmer air.
- (E) The air density inside the balloon is less than that of the surrounding air.

24. The safest and most effective emergency procedure to treat an acid splash on skin is to do which of the following immediately?

- (A) Dry the affected area with paper towels
- (B) Sprinkle the affected area with powdered  $\text{Na}_2\text{SO}_4(s)$
- (C) Flush the affected area with water and then with a dilute  $\text{NaOH}$  solution
- (D) Flush the affected area with water and then with a dilute  $\text{NaHCO}_3$  solution
- (E) Flush the affected area with water and then with a dilute vinegar solution



25. The cooling curve for a pure substance as it changes from a liquid to a solid is shown above. The solid and the liquid coexist at

(A) point *Q* only  
 (B) point *R* only  
 (C) all points on the curve between *Q* and *S*  
 (D) all points on the curve between *R* and *T*  
 (E) no point on the curve



26. When the equation above is balanced and all coefficients are reduced to their lowest whole-number terms, the coefficient for  $\text{O}_2(g)$  is

(A) 6  
 (B) 7  
 (C) 12  
 (D) 14  
 (E) 28

27. Appropriate uses of a visible-light spectrophotometer include which of the following?

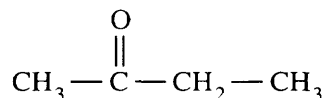
I. Determining the concentration of a solution of  $\text{Cu}(\text{NO}_3)_2$   
 II. Measuring the conductivity of a solution of  $\text{KMnO}_4$   
 III. Determining which ions are present in a solution that may contain  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$

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

28. The melting point of  $\text{MgO}$  is higher than that of  $\text{NaF}$ . Explanations for this observation include which of the following?

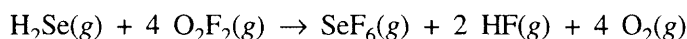
- I.  $\text{Mg}^{2+}$  is more positively charged than  $\text{Na}^+$ .
- II.  $\text{O}^{2-}$  is more negatively charged than  $\text{F}^-$ .
- III. The  $\text{O}^{2-}$  ion is smaller than the  $\text{F}^-$  ion.

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



29. The organic compound represented above is an example of

- (A) an organic acid
- (B) an alcohol
- (C) an ether
- (D) an aldehyde
- (E) a ketone



30. Which of the following is true regarding the reaction represented above?

- (A) The oxidation number of O does not change.
- (B) The oxidation number of H changes from  $-1$  to  $+1$ .
- (C) The oxidation number of F changes from  $+1$  to  $-1$ .
- (D) The oxidation number of Se changes from  $-2$  to  $+6$ .
- (E) It is a disproportionation reaction for F.

31. If the temperature of an aqueous solution of  $\text{NaCl}$  is increased from  $20^\circ\text{C}$  to  $90^\circ\text{C}$ , which of the following statements is true?

- (A) The density of the solution remains unchanged.
- (B) The molarity of the solution remains unchanged.
- (C) The molality of the solution remains unchanged.
- (D) The mole fraction of solute decreases.
- (E) The mole fraction of solute increases.

32. Types of hybridization exhibited by the C atoms in propene,  $\text{CH}_3\text{CHCH}_2$ , include which of the following?

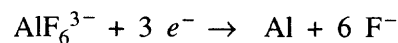
I.  $sp$   
II.  $sp^2$   
III.  $sp^3$

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

33. A 1.0 L sample of an aqueous solution contains 0.10 mol of  $\text{NaCl}$  and 0.10 mol of  $\text{CaCl}_2$ . What is the minimum number of moles of  $\text{AgNO}_3$  that must be added to the solution in order to precipitate all of the  $\text{Cl}^-$  as  $\text{AgCl}(s)$ ? (Assume that  $\text{AgCl}$  is insoluble.)

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

Questions 34-35 refer to an electrolytic cell that involves the following half-reaction.



34. Which of the following occurs in the reaction?

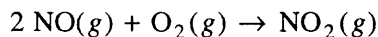
- (A)  $\text{AlF}_6^{3-}$  is reduced at the cathode.  
(B) Al is oxidized at the anode.  
(C) Aluminum is converted from the  $-3$  oxidation state to the 0 oxidation state.  
(D)  $\text{F}^-$  acts as a reducing agent.  
(E)  $\text{F}^-$  is reduced at the cathode.

35. A steady current of 10 amperes is passed through an aluminum-production cell for 15 minutes. Which of the following is the correct expression for calculating the number of grams of aluminum produced? (1 faraday = 96,500 coulombs)

- (A)  $\frac{(10)(15)(96,500)}{(27)(60)} \text{ g}$   
(B)  $\frac{(10)(15)(27)}{(60)(96,500)} \text{ g}$   
(C)  $\frac{(10)(15)(60)(27)}{(96,500)(3)} \text{ g}$   
(D)  $\frac{(96,500)(27)}{(10)(15)(60)(3)} \text{ g}$   
(E)  $\frac{(27)(3)}{(96,500)(10)(15)(60)} \text{ g}$

| Experiment | Initial [NO]<br>(mol L <sup>-1</sup> ) | Initial [O <sub>2</sub> ]<br>(mol L <sup>-1</sup> ) | Initial Rate of<br>Formation of NO <sub>2</sub><br>(mol L <sup>-1</sup> s <sup>-1</sup> ) |
|------------|----------------------------------------|-----------------------------------------------------|-------------------------------------------------------------------------------------------|
| 1          | 0.10                                   | 0.10                                                | $2.5 \times 10^{-4}$                                                                      |
| 2          | 0.20                                   | 0.10                                                | $5.0 \times 10^{-4}$                                                                      |
| 3          | 0.20                                   | 0.40                                                | $8.0 \times 10^{-3}$                                                                      |

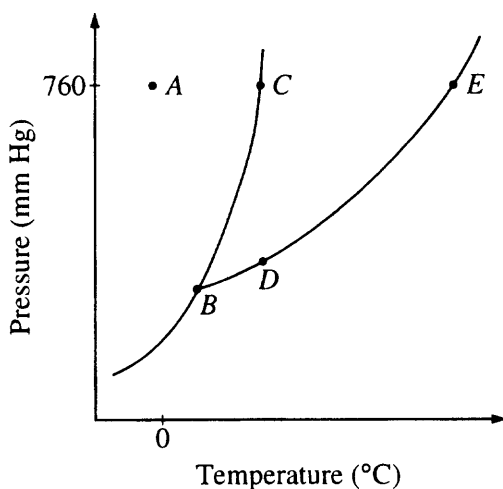
36. The initial-rate data in the table above were obtained for the reaction represented below. What is the experimental rate law for the reaction?



- (A) Rate =  $k[\text{NO}][\text{O}_2]$   
 (B) Rate =  $k[\text{NO}][\text{O}_2]^2$   
 (C) Rate =  $k[\text{NO}]^2[\text{O}_2]$   
 (D) Rate =  $k[\text{NO}]^2[\text{O}_2]^2$   
 (E) Rate =  $k \frac{[\text{NO}]}{[\text{O}_2]}$

| Ionization Energies for element X (kJ mol <sup>-1</sup> ) |        |       |        |        |
|-----------------------------------------------------------|--------|-------|--------|--------|
| First                                                     | Second | Third | Fourth | Fifth  |
| 580                                                       | 1,815  | 2,740 | 11,600 | 14,800 |

37. The ionization energies for element X are listed in the table above. On the basis of the data, element X is most likely to be
- (A) Na  
 (B) Mg  
 (C) Al  
 (D) Si  
 (E) P
38. A molecule or an ion is classified as a Lewis acid if it
- (A) accepts a proton from water  
 (B) accepts a pair of electrons to form a bond  
 (C) donates a pair of electrons to form a bond  
 (D) donates a proton to water  
 (E) has resonance Lewis electron-dot structures

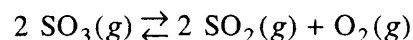


39. The phase diagram for a pure substance is shown above. Which point on the diagram corresponds to the equilibrium between the solid and liquid phases at the normal melting point?

(A) A  
(B) B  
(C) C  
(D) D  
(E) E

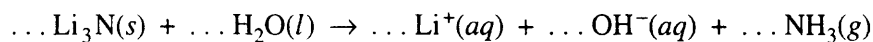
40. Of the following molecules, which has the largest dipole moment?

(A) CO  
(B) CO<sub>2</sub>  
(C) O<sub>2</sub>  
(D) HF  
(E) F<sub>2</sub>



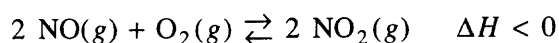
41. After the equilibrium represented above is established, some pure O<sub>2</sub>(g) is injected into the reaction vessel at constant temperature. After equilibrium is reestablished, which of the following has a lower value compared to its value at the original equilibrium?

(A)  $K_{eq}$  for the reaction  
(B) The total pressure in the reaction vessel  
(C) The amount of SO<sub>3</sub>(g) in the reaction vessel  
(D) The amount of O<sub>2</sub>(g) in the reaction vessel  
(E) The amount of SO<sub>2</sub>(g) in the reaction vessel

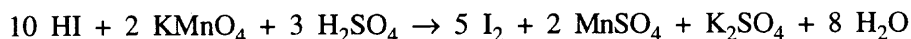


42. When the equation above is balanced and all coefficients reduced to lowest whole-number terms, the coefficient for  $\text{OH}^-(aq)$  is
- (A) 1  
(B) 2  
(C) 3  
(D) 4  
(E) 6
43. A sample of 61.8 g of  $\text{H}_3\text{BO}_3$ , a weak acid, is dissolved in 1,000 g of water to make a 1.0-molal solution. Which of the following would be the best procedure to determine the molarity of the solution? (Assume no additional information is available.)
- (A) Titration of the solution with standard acid  
(B) Measurement of the pH with a pH meter  
(C) Determination of the boiling point of the solution  
(D) Measurement of the total volume of the solution  
(E) Measurement of the specific heat of the solution
44. A rigid metal tank contains oxygen gas. Which of the following applies to the gas in the tank when additional oxygen is added at constant temperature?
- (A) The volume of the gas increases.  
(B) The pressure of the gas decreases.  
(C) The average speed of the gas molecules remains the same.  
(D) The total number of gas molecules remains the same.  
(E) The average distance between the gas molecules increases.
45. What is the  $\text{H}^+(aq)$  concentration in 0.05 M  $\text{HCN}(aq)$ ? (The  $K_a$  for HCN is  $5.0 \times 10^{-10}$ .)
- (A)  $2.5 \times 10^{-11}$  M  
(B)  $2.5 \times 10^{-10}$  M  
(C)  $5.0 \times 10^{-10}$  M  
(D)  $5.0 \times 10^{-6}$  M  
(E)  $5.0 \times 10^{-4}$  M
46. Which of the following occurs when excess concentrated  $\text{NH}_3(aq)$  is mixed thoroughly with 0.1 M  $\text{Cu}(\text{NO}_3)_2(aq)$ ?
- (A) A dark red precipitate forms and settles out.  
(B) Separate layers of immiscible liquids form with a blue layer on top.  
(C) The color of the solution turns from light blue to dark blue.  
(D) Bubbles of ammonia gas form.  
(E) The pH of the solution decreases.

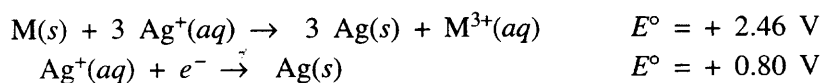
47. When hafnium metal is heated in an atmosphere of chlorine gas, the product of the reaction is found to contain 62.2 percent Hf by mass and 37.4 percent Cl by mass. What is the empirical formula for this compound?
- (A)  $\text{HfCl}$   
 (B)  $\text{HfCl}_2$   
 (C)  $\text{HfCl}_3$   
 (D)  $\text{HfCl}_4$   
 (E)  $\text{Hf}_2\text{Cl}_3$
48. If 87.5 percent of a sample of pure  $^{131}\text{I}$  decays in 24 days, what is the half-life of  $^{131}\text{I}$ ?
- (A) 6 days  
 (B) 8 days  
 (C) 12 days  
 (D) 14 days  
 (E) 21 days
49. Which of the following techniques is most appropriate for the recovery of solid  $\text{KNO}_3$  from an aqueous solution of  $\text{KNO}_3$ ?
- (A) Paper chromatography  
 (B) Filtration  
 (C) Titration  
 (D) Electrolysis  
 (E) Evaporation to dryness
50. In the periodic table, as the atomic number increases from 11 to 17, what happens to the atomic radius?
- (A) It remains constant.  
 (B) It increases only.  
 (C) It increases, then decreases.  
 (D) It decreases only.  
 (E) It decreases, then increases.
51. Which of the following is a correct interpretation of the results of Rutherford's experiments in which gold atoms were bombarded with alpha particles?
- (A) Atoms have equal numbers of positive and negative charges.  
 (B) Electrons in atoms are arranged in shells.  
 (C) Neutrons are at the center of an atom.  
 (D) Neutrons and protons in atoms have nearly equal mass.  
 (E) The positive charge of an atom is concentrated in a small region.
52. Under which of the following sets of conditions could the most  $\text{O}_2(g)$  be dissolved in  $\text{H}_2\text{O}(l)$ ?
- |     | Pressure of $\text{O}_2(g)$<br>Above $\text{H}_2\text{O}(l)$<br>(atm) | Temperature<br>of $\text{H}_2\text{O}(l)$<br>(°C) |
|-----|-----------------------------------------------------------------------|---------------------------------------------------|
| (A) | 5.0                                                                   | 80                                                |
| (B) | 5.0                                                                   | 20                                                |
| (C) | 1.0                                                                   | 80                                                |
| (D) | 1.0                                                                   | 20                                                |
| (E) | 0.5                                                                   | 20                                                |
- $\text{W}(g) + \text{X}(g) \rightarrow \text{Y}(g) + \text{Z}(g)$
53. Gases W and X react in a closed, rigid vessel to form gases Y and Z according to the equation above. The initial pressure of  $\text{W}(g)$  is 1.20 atm and that of  $\text{X}(g)$  is 1.60 atm. No  $\text{Y}(g)$  or  $\text{Z}(g)$  is initially present. The experiment is carried out at constant temperature. What is the partial pressure of  $\text{Z}(g)$  when the partial pressure of  $\text{W}(g)$  has decreased to 1.0 atm?
- (A) 0.20 atm  
 (B) 0.40 atm  
 (C) 1.0 atm  
 (D) 1.2 atm  
 (E) 1.4 atm



54. Which of the following changes alone would cause a decrease in the value of  $K_{eq}$  for the reaction represented above?
- (A) Decreasing the temperature
  - (B) Increasing the temperature
  - (C) Decreasing the volume of the reaction vessel
  - (D) Increasing the volume of the reaction vessel
  - (E) Adding a catalyst



55. According to the balanced equation above, how many moles of HI would be necessary to produce 2.5 mol of  $\text{I}_2$ , starting with 4.0 mol of  $\text{KMnO}_4$  and 3.0 mol of  $\text{H}_2\text{SO}_4$ ?
- (A) 20.
  - (B) 10.
  - (C) 8.0
  - (D) 5.0
  - (E) 2.5
56. A yellow precipitate forms when 0.5 M  $\text{NaI}(aq)$  is added to a 0.5 M solution of which of the following ions?
- (A)  $\text{Pb}^{2+}(aq)$
  - (B)  $\text{Zn}^{2+}(aq)$
  - (C)  $\text{CrO}_4^{2-}(aq)$
  - (D)  $\text{SO}_4^{2-}(aq)$
  - (E)  $\text{OH}^-(aq)$



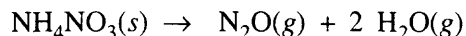
57. According to the information above, what is the standard reduction potential for the half-reaction  $\text{M}^{3+}(aq) + 3 e^- \rightarrow \text{M}(s)$ ?
- (A)  $-1.66 \text{ V}$
  - (B)  $-0.06 \text{ V}$
  - (C)  $0.06 \text{ V}$
  - (D)  $1.66 \text{ V}$
  - (E)  $3.26 \text{ V}$

58. On a mountaintop, it is observed that water boils at 90°C, not at 100°C as at sea level. This phenomenon occurs because on the mountaintop the

- (A) equilibrium water vapor pressure is higher due to the higher atmospheric pressure
- (B) equilibrium water vapor pressure is lower due to the higher atmospheric pressure
- (C) equilibrium water vapor pressure equals the atmospheric pressure at a lower temperature
- (D) water molecules have a higher average kinetic energy due to the lower atmospheric pressure
- (E) water contains a greater concentration of dissolved gases

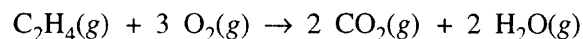
59. A 40.0 mL sample of 0.25 *M* KOH is added to 60.0 mL of 0.15 *M* Ba(OH)<sub>2</sub>. What is the molar concentration of OH<sup>−</sup>(aq) in the resulting solution? (Assume that the volumes are additive.)

- (A) 0.10 *M*
- (B) 0.19 *M*
- (C) 0.28 *M*
- (D) 0.40 *M*
- (E) 0.55 *M*



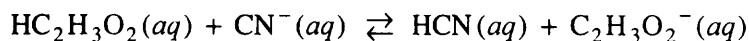
60. A 0.03 mol sample of NH<sub>4</sub>NO<sub>3</sub>(s) is placed in a 1 L evacuated flask, which is then sealed and heated. The NH<sub>4</sub>NO<sub>3</sub>(s) decomposes completely according to the balanced equation above. The total pressure in the flask measured at 400 K is closest to which of the following? (The value of the gas constant, *R*, is 0.082 L atm mol<sup>−1</sup> K<sup>−1</sup>.)

- (A) 3 atm
- (B) 1 atm
- (C) 0.5 atm
- (D) 0.1 atm
- (E) 0.03 atm

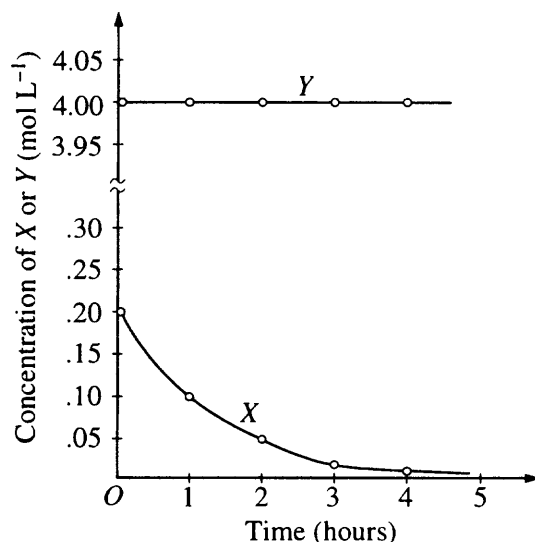


61. For the reaction of ethylene represented above, Δ*H* is −1,323 kJ. What is the value of Δ*H* if the combustion produced liquid water H<sub>2</sub>O(l), rather than water vapor H<sub>2</sub>O(g)? (Δ*H* for the phase change H<sub>2</sub>O(g) → H<sub>2</sub>O(l) is −44 kJ mol<sup>−1</sup>.)

- (A) −1,235 kJ
- (B) −1,279 kJ
- (C) −1,323 kJ
- (D) −1,367 kJ
- (E) −1,411 kJ



62. The reaction represented above has an equilibrium constant equal to  $3.7 \times 10^4$ . Which of the following can be concluded from this information?
- (A)  $\text{CN}^-(aq)$  is a stronger base than  $\text{C}_2\text{H}_3\text{O}_2^-(aq)$ .  
 (B)  $\text{HCN}(aq)$  is a stronger acid than  $\text{HC}_2\text{H}_3\text{O}_2(aq)$ .  
 (C) The conjugate base of  $\text{CN}^-(aq)$  is  $\text{C}_2\text{H}_3\text{O}_2^-(aq)$ .  
 (D) The equilibrium constant will increase with an increase in temperature.  
 (E) The pH of a solution containing equimolar amounts of  $\text{CN}^-(aq)$  and  $\text{HC}_2\text{H}_3\text{O}_2(aq)$  is 7.0.



63. The graph above shows the results of a study of the reaction of X with a large excess of Y to yield Z. The concentrations of X and Y were measured over a period of time. According to the results, which of the following can be concluded about the rate law for the reaction under the conditions studied?
- (A) It is zero order in  $[X]$ .  
 (B) It is first order in  $[X]$ .  
 (C) It is second order in  $[X]$ .  
 (D) It is first order in  $[Y]$ .  
 (E) The overall order of the reaction is 2.

64. Equal numbers of moles of He(g), Ar(g), and Ne(g) are placed in a glass vessel at room temperature. If the vessel has a pinhole-sized leak, which of the following will be true regarding the relative values of the partial pressures of the gases remaining in the vessel after some of the gas mixture has effused?

- (A)  $P_{\text{He}} < P_{\text{Ne}} < P_{\text{Ar}}$
- (B)  $P_{\text{He}} < P_{\text{Ar}} < P_{\text{Ne}}$
- (C)  $P_{\text{Ne}} < P_{\text{Ar}} < P_{\text{He}}$
- (D)  $P_{\text{Ar}} < P_{\text{He}} < P_{\text{Ne}}$
- (E)  $P_{\text{He}} = P_{\text{Ar}} = P_{\text{Ne}}$

65. Which of the following compounds is NOT appreciably soluble in water but is soluble in dilute hydrochloric acid?

- (A)  $\text{Mg}(\text{OH})_2(s)$
- (B)  $(\text{NH}_4)_2\text{CO}_3(s)$
- (C)  $\text{CuSO}_4(s)$
- (D)  $(\text{NH}_4)_2\text{SO}_4(s)$
- (E)  $\text{Sr}(\text{NO}_3)_2(s)$

66. When solid ammonium chloride,  $\text{NH}_4\text{Cl}(s)$ , is added to water at  $25^\circ\text{C}$ , it dissolves and the temperature of the solution decreases. Which of the following is true for the values of  $\Delta H$  and  $\Delta S$  for the dissolving process?

- | $\Delta H$   | $\Delta S$    |
|--------------|---------------|
| (A) Positive | Positive      |
| (B) Positive | Negative      |
| (C) Positive | Equal to zero |
| (D) Negative | Positive      |
| (E) Negative | Negative      |

67. What is the molar solubility in water of  $\text{Ag}_2\text{CrO}_4$  ?

(The  $K_{sp}$  for  $\text{Ag}_2\text{CrO}_4$  is  $8 \times 10^{-12}$ .)

- (A)  $8 \times 10^{-12} M$
- (B)  $2 \times 10^{-12} M$
- (C)  $\sqrt{4 \times 10^{-12}} M$
- (D)  $\sqrt[3]{4 \times 10^{-12}} M$
- (E)  $\sqrt[3]{2 \times 10^{-12}} M$

68. In which of the following processes are covalent bonds broken?
- (A)  $\text{I}_2(s) \rightarrow \text{I}_2(g)$
  - (B)  $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$
  - (C)  $\text{NaCl}(s) \rightarrow \text{NaCl}(l)$
  - (D)  $\text{C}(\text{diamond}) \rightarrow \text{C}(g)$
  - (E)  $\text{Fe}(s) \rightarrow \text{Fe}(l)$
69. What is the final concentration of barium ions,  $[\text{Ba}^{2+}]$ , in solution when 100. mL of 0.10 *M*  $\text{BaCl}_2(aq)$  is mixed with 100. mL of 0.050 *M*  $\text{H}_2\text{SO}_4(aq)$ ?
- (A) 0.00 *M*
  - (B) 0.012 *M*
  - (C) 0.025 *M*
  - (D) 0.075 *M*
  - (E) 0.10 *M*
70. When 100 mL of 1.0 *M*  $\text{Na}_3\text{PO}_4$  is mixed with 100 mL of 1.0 *M*  $\text{AgNO}_3$ , a yellow precipitate forms and  $[\text{Ag}^+]$  becomes negligibly small. Which of the following is a correct listing of the ions remaining in solution in order of increasing concentration?
- (A)  $[\text{PO}_4^{3-}] < [\text{NO}_3^-] < [\text{Na}^+]$
  - (B)  $[\text{PO}_4^{3-}] < [\text{Na}^+] < [\text{NO}_3^-]$
  - (C)  $[\text{NO}_3^-] < [\text{PO}_4^{3-}] < [\text{Na}^+]$
  - (D)  $[\text{Na}^+] < [\text{NO}_3^-] < [\text{PO}_4^{3-}]$
  - (E)  $[\text{Na}^+] < [\text{PO}_4^{3-}] < [\text{NO}_3^-]$
71. In a qualitative analysis for the presence of  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Cu}^{2+}$  ions in aqueous solution, which of the following will allow the separation of  $\text{Pb}^{2+}$  from the other ions at room temperature?
- (A) Adding dilute  $\text{Na}_2\text{S}(aq)$  solution
  - (B) Adding dilute  $\text{HCl}(aq)$  solution
  - (C) Adding dilute  $\text{NaOH}(aq)$  solution
  - (D) Adding dilute  $\text{NH}_3(aq)$  solution
  - (E) Adding dilute  $\text{HNO}_3(aq)$  solution
72. After completing an experiment to determine gravimetrically the percentage of water in a hydrate, a student reported a value of 38 percent. The correct value for the percentage of water in the hydrate is 51 percent. Which of the following is the most likely explanation for this difference?
- (A) Strong initial heating caused some of the hydrate sample to spatter out of the crucible.
  - (B) The dehydrated sample absorbed moisture after heating.
  - (C) The amount of the hydrate sample used was too small.
  - (D) The crucible was not heated to constant mass before use.
  - (E) Excess heating caused the dehydrated sample to decompose.

73. The volume of distilled water that should be added to 10.0 mL of 6.00 M  $\text{HCl}(aq)$  in order to prepare a 0.500 M  $\text{HCl}(aq)$  solution is approximately
- (A) 50.0 mL
  - (B) 60.0 mL
  - (C) 100. mL
  - (D) 110. mL
  - (E) 120. mL
74. Which of the following gases deviates most from ideal behavior?
- (A)  $\text{SO}_2$
  - (B) Ne
  - (C)  $\text{CH}_4$
  - (D)  $\text{N}_2$
  - (E)  $\text{H}_2$
75. Which of the following pairs of liquids forms the solution that is most ideal (most closely follows Raoult's law) ?
- (A)  $\text{C}_8\text{H}_{18}(l)$  and  $\text{H}_2\text{O}(l)$
  - (B)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(l)$  and  $\text{H}_2\text{O}(l)$
  - (C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(l)$  and  $\text{C}_8\text{H}_{18}(l)$
  - (D)  $\text{C}_6\text{H}_{14}(l)$  and  $\text{C}_8\text{H}_{18}(l)$
  - (E)  $\text{H}_2\text{SO}_4(l)$  and  $\text{H}_2\text{O}(l)$

END OF SECTION I

IF YOU FINISH BEFORE TIME IS CALLED, YOU MAY CHECK YOUR WORK ON THIS SECTION.  
DO NOT GO ON TO SECTION II UNTIL YOU ARE TOLD TO DO SO.

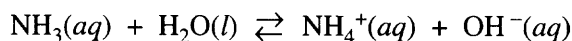
**CHEMISTRY—SECTION II**  
(Total time—90 minutes)

**Part A**  
Time—40 minutes

**YOU MAY USE YOUR CALCULATOR FOR PART A.**

CLEARLY SHOW THE METHOD USED AND STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, because you may earn 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 1 below. The Section II score weighting for this question is 20 percent.



1. In aqueous solution, ammonia reacts as represented above. In  $0.0180\text{ M NH}_3(aq)$  at  $25^\circ\text{C}$ , the hydroxide ion concentration,  $[\text{OH}^-]$ , is  $5.60 \times 10^{-4}\text{ M}$ . In answering the following, assume that temperature is constant at  $25^\circ\text{C}$  and that volumes are additive.
- (a) Write the equilibrium-constant expression for the reaction represented above.
  - (b) Determine the pH of  $0.0180\text{ M NH}_3(aq)$ .
  - (c) Determine the value of the base ionization constant,  $K_b$ , for  $\text{NH}_3(aq)$ .
  - (d) Determine the percent ionization of  $\text{NH}_3$  in  $0.0180\text{ M NH}_3(aq)$ .
  - (e) In an experiment, a  $20.0\text{ mL}$  sample of  $0.0180\text{ M NH}_3(aq)$  was placed in a flask and titrated to the equivalence point and beyond using  $0.0120\text{ M HCl}(aq)$ .
    - (i) Determine the volume of  $0.0120\text{ M HCl}(aq)$  that was added to reach the equivalence point.
    - (ii) Determine the pH of the solution in the flask after a total of  $15.0\text{ mL}$  of  $0.0120\text{ M HCl}(aq)$  was added.
    - (iii) Determine the pH of the solution in the flask after a total of  $40.0\text{ mL}$  of  $0.0120\text{ M HCl}(aq)$  was added.

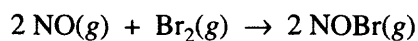
**GO ON TO THE NEXT PAGE** 

Answer EITHER Question 2 below OR Question 3 on the next page. 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 you choose is 20 percent.

2. Answer the following questions regarding light and its interactions with molecules, atoms, and ions.

- (a) The longest wavelength of light with enough energy to break the Cl–Cl bond in  $\text{Cl}_2(g)$  is 495 nm.
- (i) Calculate the frequency, in  $\text{s}^{-1}$ , of the light.
  - (ii) Calculate the energy, in J, of a photon of the light.
  - (iii) Calculate the minimum energy, in  $\text{kJ mol}^{-1}$ , of the Cl–Cl bond.
- (b) A certain line in the spectrum of atomic hydrogen is associated with the electronic transition in the H atom from the sixth energy level ( $n = 6$ ) to the second energy level ( $n = 2$ ).
- (i) Indicate whether the H atom emits energy or whether it absorbs energy during the transition. Justify your answer.
  - (ii) Calculate the wavelength, in nm, of the radiation associated with the spectral line.
  - (iii) Account for the observation that the amount of energy associated with the same electronic transition ( $n = 6$  to  $n = 2$ ) in the  $\text{He}^+$  ion is greater than that associated with the corresponding transition in the H atom.

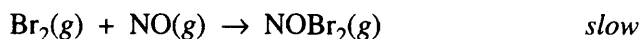
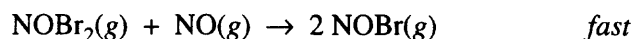
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3. A rate study of the reaction represented above was conducted at 25°C. The data that were obtained are shown in the table below.

| Experiment | Initial [NO]<br>(mol L <sup>-1</sup> ) | Initial [Br <sub>2</sub> ]<br>(mol L <sup>-1</sup> ) | Initial Rate of<br>Appearance of<br>NOBr<br>(mol L <sup>-1</sup> s <sup>-1</sup> ) |
|------------|----------------------------------------|------------------------------------------------------|------------------------------------------------------------------------------------|
| 1          | 0.0160                                 | 0.0120                                               | $3.24 \times 10^{-4}$                                                              |
| 2          | 0.0160                                 | 0.0240                                               | $6.38 \times 10^{-4}$                                                              |
| 3          | 0.0320                                 | 0.0060                                               | $6.42 \times 10^{-4}$                                                              |

- (a) Calculate the initial rate of disappearance of Br<sub>2</sub>(g) in experiment 1.
- (b) Determine the order of the reaction with respect to each reactant, Br<sub>2</sub>(g) and NO(g). In each case, explain your reasoning.
- (c) For the reaction,
- write the rate law that is consistent with the data, and
  - calculate the value of the specific rate constant, k, and specify units.
- (d) The following mechanism was proposed for the reaction:



Is this mechanism consistent with the given experimental observations? Justify your answer.

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## CHEMISTRY

## Part B

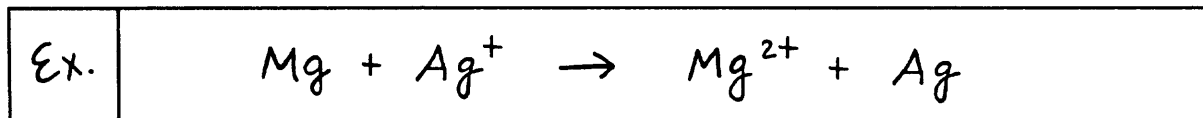
Time—50 minutes

NO CALCULATORS MAY BE USED WITH PART B.

Answer Question 4 below. The Section II score weighting for this question is 15 percent.

4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. 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.

Example: A strip of magnesium is added to a solution of silver nitrate.

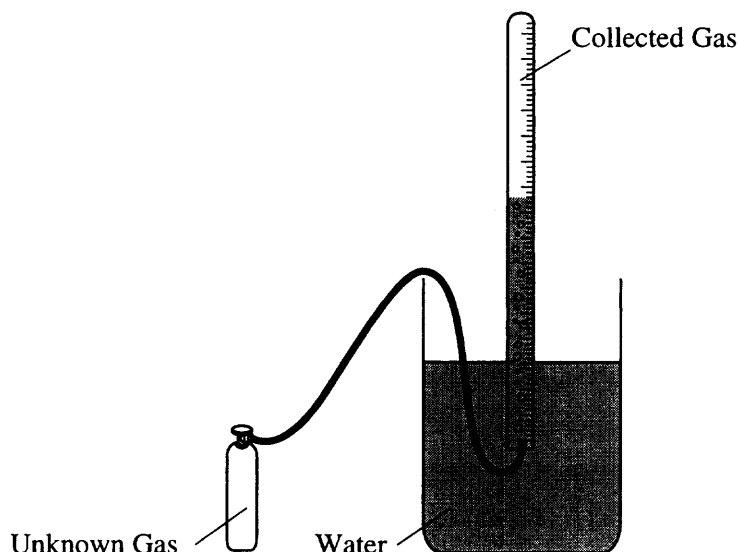


- (a) Calcium oxide powder is added to distilled water.
- (b) Solid ammonium nitrate is heated to temperatures above 300°C.
- (c) Liquid bromine is shaken with a 0.5 *M* sodium iodide solution.
- (d) Solid lead(II) carbonate is added to a 0.5 *M* sulfuric acid solution.
- (e) A mixture of powdered iron(III) oxide and powdered aluminum metal is heated strongly.
- (f) Methylamine gas is bubbled into distilled water.
- (g) Carbon dioxide gas is passed over hot, solid sodium oxide.
- (h) A 0.2 *M* barium nitrate solution is added to an alkaline 0.2 *M* potassium chromate solution.

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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.

Answer BOTH Question 5 below AND Question 6 on the next page. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

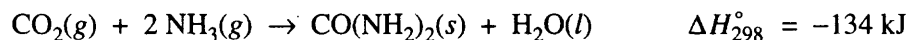


5. A student performs an experiment to determine the molar mass of an unknown gas. A small amount of the pure gas is released from a pressurized container and collected in a graduated tube over water at room temperature, as shown in the diagram above. The collection tube containing the gas is allowed to stand for several minutes, and its depth is adjusted until the water levels inside and outside the tube are the same. Assume that:
- the gas is not appreciably soluble in water
  - the gas collected in the graduated tube and the water are in thermal equilibrium
  - a barometer, a thermometer, an analytical balance, and a table of the equilibrium vapor pressure of water at various temperatures are also available.
- (a) Write the equation(s) needed to calculate the molar mass of the gas.
- (b) List the measurements that must be made in order to calculate the molar mass of the gas.
- (c) Explain the purpose of equalizing the water levels inside and outside the gas collection tube.
- (d) The student determines the molar mass of the gas to be  $64 \text{ g mol}^{-1}$ . Write the expression (set-up) for calculating the percent error in the experimental value, assuming that the unknown gas is butane (molar mass  $58 \text{ g mol}^{-1}$ ). Calculations are not required.
- (e) If the student fails to use information from the table of the equilibrium vapor pressures of water in the calculation, the calculated value for the molar mass of the unknown gas will be smaller than the actual value. Explain.

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6. Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory.

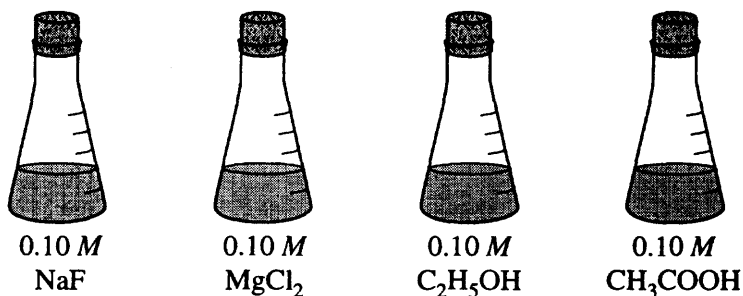
(a) Consider the reaction represented below, which is spontaneous at 298 K.



- (i) For the reaction, indicate whether the standard entropy change,  $\Delta S_{298}^\circ$ , is positive, or negative, or zero. Justify your answer.
  - (ii) Which factor, the change in enthalpy,  $\Delta H_{298}^\circ$ , or the change in entropy,  $\Delta S_{298}^\circ$ , provides the principal driving force for the reaction at 298 K? Explain.
  - (iii) For the reaction, how is the value of the standard free energy change,  $\Delta G^\circ$ , affected by an increase in temperature? Explain.
- (b) Some reactions that are predicted by their sign of  $\Delta G^\circ$  to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.
- (i) Account for this apparent contradiction.
  - (ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on  $\Delta G^\circ$  for the reaction? Explain.

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Answer EITHER Question 7 OR Question 8 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 you choose is 15 percent.



7. Answer the following questions, which refer to the 100 mL samples of aqueous solutions at  $25^\circ\text{C}$  in the stoppered flasks shown above.
- (a) Which solution has the lowest electrical conductivity? Explain.
  - (b) Which solution has the lowest freezing point? Explain.
  - (c) Above which solution is the pressure of water vapor greatest? Explain.
  - (d) Which solution has the highest pH? Explain.
8. Answer the following questions using principles of chemical bonding and molecular structure.
- (a) Consider the carbon dioxide molecule,  $\text{CO}_2$ , and the carbonate ion,  $\text{CO}_3^{2-}$ .
    - (i) Draw the complete Lewis electron-dot structure for each species.
    - (ii) Account for the fact that the carbon-oxygen bond length in  $\text{CO}_3^{2-}$  is greater than the carbon-oxygen bond length in  $\text{CO}_2$ .
  - (b) Consider the molecules  $\text{CF}_4$  and  $\text{SF}_4$ .
    - (i) Draw the complete Lewis electron-dot structure for each molecule.
    - (ii) In terms of molecular geometry, account for the fact that the  $\text{CF}_4$  molecule is nonpolar, whereas the  $\text{SF}_4$  molecule is polar.

**END OF EXAMINATION**

# PERIODIC TABLE OF THE ELEMENTS

|                           |                           |                            |                            |                            |                            |                            |                            |                            |                           |                           |                           |                           |                           |                           |                           |                           |                           |
|---------------------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 1<br><b>H</b><br>1.0079   |                           |                            |                            |                            |                            |                            |                            |                            |                           |                           |                           |                           |                           |                           |                           |                           | 2<br><b>He</b><br>4.0026  |
| 3<br><b>Li</b><br>6.941   | 4<br><b>Be</b><br>9.012   |                            |                            |                            |                            |                            |                            |                            |                           |                           |                           | 5<br><b>B</b><br>10.811   | 6<br><b>C</b><br>12.011   | 7<br><b>N</b><br>14.007   | 8<br><b>O</b><br>16.00    | 9<br><b>F</b><br>19.00    | 10<br><b>Ne</b><br>20.179 |
| 11<br><b>Na</b><br>22.99  | 12<br><b>Mg</b><br>24.30  |                            |                            |                            |                            |                            |                            |                            |                           |                           |                           | 13<br><b>Al</b><br>26.98  | 14<br><b>Si</b><br>28.09  | 15<br><b>P</b><br>30.974  | 16<br><b>S</b><br>32.06   | 17<br><b>Cl</b><br>35.453 | 18<br><b>Ar</b><br>39.948 |
| 19<br><b>K</b><br>39.10   | 20<br><b>Ca</b><br>40.08  | 21<br><b>Sc</b><br>44.96   | 22<br><b>Ti</b><br>47.90   | 23<br><b>V</b><br>50.94    | 24<br><b>Cr</b><br>52.00   | 25<br><b>Mn</b><br>54.938  | 26<br><b>Fe</b><br>55.85   | 27<br><b>Co</b><br>58.93   | 28<br><b>Ni</b><br>58.69  | 29<br><b>Cu</b><br>63.55  | 30<br><b>Zn</b><br>65.39  | 31<br><b>Ga</b><br>69.72  | 32<br><b>Ge</b><br>72.59  | 33<br><b>As</b><br>74.92  | 34<br><b>Se</b><br>78.96  | 35<br><b>Br</b><br>79.90  | 36<br><b>Kr</b><br>83.80  |
| 37<br><b>Rb</b><br>85.47  | 38<br><b>Sr</b><br>87.62  | 39<br><b>Y</b><br>88.91    | 40<br><b>Zr</b><br>91.22   | 41<br><b>Nb</b><br>92.91   | 42<br><b>Mo</b><br>95.94   | 43<br><b>Tc</b><br>(98)    | 44<br><b>Ru</b><br>101.1   | 45<br><b>Rh</b><br>102.91  | 46<br><b>Pd</b><br>106.42 | 47<br><b>Ag</b><br>107.87 | 48<br><b>Cd</b><br>112.41 | 49<br><b>In</b><br>114.82 | 50<br><b>Sn</b><br>118.71 | 51<br><b>Sb</b><br>121.75 | 52<br><b>Te</b><br>127.60 | 53<br><b>I</b><br>126.91  | 54<br><b>Xe</b><br>131.29 |
| 55<br><b>Cs</b><br>132.91 | 56<br><b>Ba</b><br>137.33 | 57<br><b>*La</b><br>138.91 | 72<br><b>Hf</b><br>178.49  | 73<br><b>Ta</b><br>180.95  | 74<br><b>W</b><br>183.85   | 75<br><b>Re</b><br>186.21  | 76<br><b>Os</b><br>190.2   | 77<br><b>Ir</b><br>192.2   | 78<br><b>Pt</b><br>195.08 | 79<br><b>Au</b><br>196.97 | 80<br><b>Hg</b><br>200.59 | 81<br><b>Tl</b><br>204.38 | 82<br><b>Pb</b><br>207.2  | 83<br><b>Bi</b><br>208.98 | 84<br><b>Po</b><br>(209)  | 85<br><b>At</b><br>(210)  | 86<br><b>Rn</b><br>(222)  |
| 87<br><b>Fr</b><br>(223)  | 88<br><b>Ra</b><br>226.02 | 89<br><b>†Ac</b><br>227.03 | 104<br><b>Unq</b><br>(261) | 105<br><b>Unp</b><br>(262) | 106<br><b>Unh</b><br>(263) | 107<br><b>Uns</b><br>(262) | 108<br><b>Uno</b><br>(265) | 109<br><b>Une</b><br>(266) |                           |                           |                           |                           |                           |                           |                           |                           |                           |

\*Lanthanide Series:

|                           |                           |                           |                          |                          |                           |                           |                           |                           |                           |                           |                           |                           |                           |
|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 58<br><b>Ce</b><br>140.12 | 59<br><b>Pr</b><br>140.91 | 60<br><b>Nd</b><br>144.24 | 61<br><b>Pm</b><br>(145) | 62<br><b>Sm</b><br>150.4 | 63<br><b>Eu</b><br>151.97 | 64<br><b>Gd</b><br>157.25 | 65<br><b>Tb</b><br>158.93 | 66<br><b>Dy</b><br>162.50 | 67<br><b>Ho</b><br>164.93 | 68<br><b>Er</b><br>167.26 | 69<br><b>Tm</b><br>168.93 | 70<br><b>Yb</b><br>173.04 | 71<br><b>Lu</b><br>174.97 |
|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|

†Actinide Series:

|                           |                           |                          |                           |                          |                          |                          |                          |                          |                          |                           |                           |                           |                           |
|---------------------------|---------------------------|--------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 90<br><b>Th</b><br>232.04 | 91<br><b>Pa</b><br>231.04 | 92<br><b>U</b><br>238.03 | 93<br><b>Np</b><br>237.05 | 94<br><b>Pu</b><br>(244) | 95<br><b>Am</b><br>(243) | 96<br><b>Cm</b><br>(247) | 97<br><b>Bk</b><br>(247) | 98<br><b>Cf</b><br>(251) | 99<br><b>Es</b><br>(252) | 100<br><b>Fm</b><br>(257) | 101<br><b>Md</b><br>(258) | 102<br><b>No</b><br>(259) | 103<br><b>Lr</b><br>(260) |
|---------------------------|---------------------------|--------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|

## STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

| Half-reaction                                                              |  | $E^\circ(\text{V})$ |
|----------------------------------------------------------------------------|--|---------------------|
| $\text{Li}^+ + e^- \rightarrow \text{Li}(s)$                               |  | -3.05               |
| $\text{Cs}^+ + e^- \rightarrow \text{Cs}(s)$                               |  | -2.92               |
| $\text{K}^+ + e^- \rightarrow \text{K}(s)$                                 |  | -2.92               |
| $\text{Rb}^+ + e^- \rightarrow \text{Rb}(s)$                               |  | -2.92               |
| $\text{Ba}^{2+} + 2 e^- \rightarrow \text{Ba}(s)$                          |  | -2.90               |
| $\text{Sr}^{2+} + 2 e^- \rightarrow \text{Sr}(s)$                          |  | -2.89               |
| $\text{Ca}^{2+} + 2 e^- \rightarrow \text{Ca}(s)$                          |  | -2.87               |
| $\text{Na}^+ + e^- \rightarrow \text{Na}(s)$                               |  | -2.71               |
| $\text{Mg}^{2+} + 2 e^- \rightarrow \text{Mg}(s)$                          |  | -2.37               |
| $\text{Be}^{2+} + 2 e^- \rightarrow \text{Be}(s)$                          |  | -1.70               |
| $\text{Al}^{3+} + 3 e^- \rightarrow \text{Al}(s)$                          |  | -1.66               |
| $\text{Mn}^{2+} + 2 e^- \rightarrow \text{Mn}(s)$                          |  | -1.18               |
| $\text{Zn}^{2+} + 2 e^- \rightarrow \text{Zn}(s)$                          |  | -0.76               |
| $\text{Cr}^{3+} + 3 e^- \rightarrow \text{Cr}(s)$                          |  | -0.74               |
| $\text{Fe}^{2+} + 2 e^- \rightarrow \text{Fe}(s)$                          |  | -0.44               |
| $\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$                          |  | -0.41               |
| $\text{Cd}^{2+} + 2 e^- \rightarrow \text{Cd}(s)$                          |  | -0.40               |
| $\text{Tl}^+ + e^- \rightarrow \text{Tl}(s)$                               |  | -0.34               |
| $\text{Co}^{2+} + 2 e^- \rightarrow \text{Co}(s)$                          |  | -0.28               |
| $\text{Ni}^{2+} + 2 e^- \rightarrow \text{Ni}(s)$                          |  | -0.25               |
| $\text{Sn}^{2+} + 2 e^- \rightarrow \text{Sn}(s)$                          |  | -0.14               |
| $\text{Pb}^{2+} + 2 e^- \rightarrow \text{Pb}(s)$                          |  | -0.13               |
| $2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2(g)$                           |  | 0.00                |
| $\text{S}(s) + 2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\text{S}(g)$     |  | 0.14                |
| $\text{Sn}^{4+} + 2 e^- \rightarrow \text{Sn}^{2+}$                        |  | 0.15                |
| $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$                             |  | 0.15                |
| $\text{Cu}^{2+} + 2 e^- \rightarrow \text{Cu}(s)$                          |  | 0.34                |
| $\text{Cu}^+ + e^- \rightarrow \text{Cu}(s)$                               |  | 0.52                |
| $\text{I}_2(s) + 2 e^- \rightarrow 2 \text{I}^-$                           |  | 0.53                |
| $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$                          |  | 0.77                |
| $\text{Hg}_2^{2+} + 2 e^- \rightarrow 2 \text{Hg}(l)$                      |  | 0.79                |
| $\text{Ag}^+ + e^- \rightarrow \text{Ag}(s)$                               |  | 0.80                |
| $\text{Hg}^{2+} + 2 e^- \rightarrow \text{Hg}(l)$                          |  | 0.85                |
| $2 \text{Hg}^{2+} + 2 e^- \rightarrow \text{Hg}_2^{2+}$                    |  | 0.92                |
| $\text{Br}_2(l) + 2 e^- \rightarrow 2 \text{Br}^-$                         |  | 1.07                |
| $\text{O}_2(g) + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O}(l)$ |  | 1.23                |
| $\text{Cl}_2(g) + 2 e^- \rightarrow 2 \text{Cl}^-$                         |  | 1.36                |
| $\text{Au}^{3+} + 3 e^- \rightarrow \text{Au}(s)$                          |  | 1.50                |
| $\text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+}$                          |  | 1.82                |
| $\text{F}_2(g) + 2 e^- \rightarrow 2 \text{F}^-$                           |  | 2.87                |

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# ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

## ATOMIC STRUCTURE

$$\Delta E = h\nu$$

$$c = \lambda\nu$$

$$\lambda = \frac{h}{m\nu}$$

$$p = m\nu$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

$E$  = energy

$\nu$  = frequency

$\lambda$  = wavelength

$p$  = momentum

$\nu$  = velocity

$n$  = principal quantum number

$m$  = mass

## EQUILIBRIUM

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

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

$$K_w = [\text{OH}^-][\text{H}^+] = 1.0 \times 10^{-14} \text{ @ } 25^\circ\text{C}$$

$$= K_a \times K_b$$

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

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

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

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

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

$$K_p = K_c(RT)^{\Delta n},$$

where  $\Delta n$  = moles product gas – moles reactant gas

$$\text{Speed of light, } c = 3.0 \times 10^8 \text{ m s}^{-1}$$

$$\text{Planck's constant, } h = 6.63 \times 10^{-34} \text{ J s}$$

$$\text{Boltzmann's constant, } k = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$\text{Avogadro's number} = 6.022 \times 10^{23} \text{ molecules mol}^{-1}$$

$$\text{Electron charge, } e = -1.602 \times 10^{-19} \text{ coulomb}$$

$$1 \text{ electron volt per atom} = 96.5 \text{ kJ mol}^{-1}$$

## Equilibrium Constants

$K_a$  (weak acid)

$K_b$  (weak base)

$K_w$  (water)

$K_p$  (gas pressure)

$K_c$  (molar concentrations)

$S^\circ$  = standard entropy

$H^\circ$  = standard enthalpy

$G^\circ$  = standard free energy

$E^\circ$  = standard reduction potential

$T$  = temperature

$n$  = moles

$m$  = mass

$q$  = heat

$c$  = specific heat capacity

$C_p$  = molar heat capacity at constant pressure

1 faraday  $\mathcal{F}$  = 96,500 coulombs

## THERMOCHEMISTRY

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

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

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

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

$$= -RT \ln K = -2.303 RT \log K$$

$$= -n \mathcal{F} E^\circ$$

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

$$q = mc\Delta T$$

$$C_p = \frac{\Delta H}{\Delta T}$$

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## GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$D = \frac{m}{V}$$

$$u_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

$$KE \text{ per molecule} = \frac{1}{2} mv^2$$

$$KE \text{ per mole} = \frac{3}{2} RTn$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

molarity,  $M$  = moles solute per liter solution

molality = moles solute per kilogram solvent

$$\Delta T_f = iK_f \times \text{molality}$$

$$\Delta T_b = iK_b \times \text{molality}$$

$$\pi = \frac{nRT}{V} i$$

$P$  = pressure

$V$  = volume

$T$  = temperature

$n$  = number of moles

$D$  = density

$m$  = mass

$v$  = velocity

$u_{\text{rms}}$  = root-mean-square speed

$KE$  = kinetic energy

$r$  = rate of effusion

$M$  = molar mass

$\pi$  = osmotic pressure

$i$  = van't Hoff factor

$K_f$  = molal freezing-point depression constant

$K_b$  = molal boiling-point elevation constant

$Q$  = reaction quotient

$I$  = current (amperes)

$q$  = charge (coulombs)

$t$  = time (seconds)

$E^\circ$  = standard reduction potential

$K$  = equilibrium constant

Gas constant,  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

$= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$

Boltzmann's constant,  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

$K_f$  for  $\text{H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$

$K_b$  for  $\text{H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$

STP =  $0.000^\circ\text{C}$  and  $1.000 \text{ atm}$

Faraday's constant,  $\mathcal{F} = 96,500 \text{ coulombs per mole of electrons}$

## OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

$$I = \frac{q}{t}$$

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

$$\log K = \frac{nE^\circ}{0.0592}$$

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# APPENDIX - ANSWERS

## AP CHEMISTRY 1999

Multiple-choice key transcribed from the matching supplied source.

| Question | Answer | Question | Answer | Question | Answer |
|----------|--------|----------|--------|----------|--------|
| 1        | C      | 26       | C      | 51       | E      |
| 2        | E      | 27       | A      | 52       | B      |
| 3        | B      | 28       | B      | 53       | A      |
| 4        | A      | 29       | E      | 54       | B      |
| 5        | D      | 30       | D      | 55       | D      |
| 6        | A      | 31       | C      | 56       | A      |
| 7        | C      | 32       | D      | 57       | A      |
| 8        | E      | 33       | C      | 58       | C      |
| 9        | C      | 34       | A      | 59       | C      |
| 10       | E      | 35       | C      | 60       | A      |
| 11       | A      | 36       | B      | 61       | E      |
| 12       | B      | 37       | C      | 62       | A      |
| 13       | A      | 38       | B      | 63       | B      |
| 14       | B      | 39       | C      | 64       | A      |
| 15       | D      | 40       | D      | 65       | A      |
| 16       | C      | 41       | E      | 66       | A      |
| 17       | E      | 42       | C      | 67       | E      |
| 18       | A      | 43       | D      | 68       | D      |
| 19       | C      | 44       | C      | 69       | C      |
| 20       | B      | 45       | D      | 70       | A      |
| 21       | B      | 46       | C      | 71       | B      |
| 22       | E      | 47       | C      | 72       | B      |
| 23       | E      | 48       | B      | 73       | D      |
| 24       | D      | 49       | E      | 74       | A      |
| 25       | C      | 50       | D      | 75       | D      |

Optional FRQs retain the original exam selection instructions.

## Scoring Guidelines for Free-Response Question 1

### Question 1 (9 points)

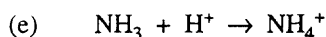
(a)  $K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$  1 pt

(b)  $[\text{OH}^-] = 5.60 \times 10^{-4} \Rightarrow \left\{ \begin{array}{l} \text{pOH} = 3.252 \\ \text{or} \\ [\text{H}^+] = 1.79 \times 10^{-11} \end{array} \right\} \Rightarrow \text{pH} = 10.748$  1 pt

(c)  $K_b = \frac{(5.60 \times 10^{-4})^2}{0.0180 - 5.60 \times 10^{-4}} = 1.74 \times 10^{-5} \text{ (or } 1.80 \times 10^{-5})$  2 pts

Note: 1<sup>st</sup> point for  $[\text{NH}_4^+] = [\text{OH}^-] = 5.60 \times 10^{-4}$ ; 2<sup>nd</sup> point for correct answer

(d)  $\% \text{ ionization} = \frac{5.60 \times 10^{-4}}{0.0180} \times 100\% = 3.11\% \text{ (or } 0.0311)$  1 pt



(i)  $\text{mol NH}_3 = 0.0180 \text{ M} \times 0.0200 \text{ L} = 3.60 \times 10^{-4} \text{ mol} = \text{mol H}^+ \text{ needed}$

$\text{vol HCl solution} = \frac{3.60 \times 10^{-4} \text{ mol}}{0.0120 \text{ M}} = 0.0300 \text{ L} = 30.0 \text{ mL}$  1 pt

(ii)  $\text{mol H}^+ \text{ added} = \text{mol } 0.0120 \text{ M} \times 0.0150 \text{ L} = 1.80 \times 10^{-4} \text{ mol H}^+ \text{ added}$   
 $= 1.80 \times 10^{-4} \text{ mol NH}_4^+ \text{ produced}$

$[\text{NH}_4^+] = \frac{1.80 \times 10^{-4} \text{ mol}}{0.0350 \text{ L}} = 0.00514 \text{ M} = [\text{NH}_3]$  1 pt

Note: Point earned for  $1.80 \times 10^{-4} \text{ mol}$ , or  $0.00514 \text{ M}$   $[\text{NH}_3]$  or  $[\text{NH}_4^+]$ , or statement “halfway to equivalence point”.

$K_b = 1.80 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{OH}^-] \Rightarrow \text{pOH} = 4.745 \Rightarrow \text{pH} = 9.255$  1 pt  
 $(= 1.74 \times 10^{-5}) \qquad \qquad \qquad (= 4.759) \qquad \qquad (= 9.241)$

(iii) 10.0 mL past equivalence point

$0.0100 \text{ L} \times 0.0120 \text{ M} = 1.20 \times 10^{-4} \text{ mol H}^+ \text{ in } 60.0 \text{ mL}$

$[\text{H}^+] = \frac{0.000120 \text{ mol}}{0.0600 \text{ L}} = 0.00200 \text{ M}$

$\text{pH} = -\log(2.00 \times 10^{-3}) = 2.700$  1 pt

---

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures\* (maximum once per question)

\*number of significant figures must be correct within  $\pm$  one digit (except for pH:  $\pm$  two digits)

## Scoring Guidelines for Free-Response Question 2

### Question 2

(9 points)

(a) (i)  $\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/sec}}{495 \text{ nm}} \text{ (or, } = \frac{3.00 \times 10^8 \text{ m/sec}}{495 \times 10^{-9} \text{ m}}) = 6.06 \times 10^{14} \text{ sec}^{-1}$  1 pt

(ii)  $E = h\nu = (6.626 \times 10^{-34} \text{ J sec})(6.06 \times 10^{14} \text{ sec}^{-1}) = 4.02 \times 10^{-19} \text{ J}$  1 pt

(iii)  $(4.02 \times 10^{-19} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})(0.00100 \text{ kJ/J}) = 242 \text{ kJ/mol}$  1 pt

Note: No units required if answers are numerically same as above. No penalty if answers are correct with different units and units are explicitly indicated (e.g., for part (ii),  $4.02 \times 10^{-22} \text{ kJ}$  is acceptable)

(b) (i) Energy is emitted. 1 pt

The  $n = 6$  state is at a higher energy than the  $n = 2$  state. Going from a high energy state to a low energy state means that energy must be emitted. 1 pt

Note: The key idea is that the energy of the  $n = 6$  state is higher (more excited) than the lower (less excited)  $n = 2$  state. The argument that “ $e^-$  is farther away” at the  $n = 6$  level is not accepted.

(ii)  $E_2 = \frac{-2.178 \times 10^{-18} \text{ J}}{2^2} = -5.45 \times 10^{-19} \text{ J}, \quad E_6 = \frac{-2.178 \times 10^{-18} \text{ J}}{6^2} = -6.05 \times 10^{-20} \text{ J}$   
 $\Delta E = E_6 - E_2 = -6.05 \times 10^{-20} \text{ J} - (-5.45 \times 10^{-19} \text{ J}) = 4.84 \times 10^{-19} \text{ J}$

OR, 1 pt

$$\Delta E = 2.178 \times 10^{-18} \left( \frac{1}{2^2} - \frac{1}{6^2} \right) \text{ J} = 2.178 \times 10^{-18} (0.2222) \text{ J} = 4.84 \times 10^{-19} \text{ J}$$

Note: Point earned for determining the energy of transition.  
 Negative energies acceptable.

$$E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

OR, 1 pt

$$\nu = \frac{E}{h} = \frac{4.84 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J sec}} = 7.30 \times 10^{14} \text{ sec}^{-1}$$

Note: Point earned for writing or using  $E = \frac{hc}{\lambda}$ , or for calculating the frequency,  $\nu$

## Scoring Guidelines for Free-Response Question 2 (continued)

(ii) *continued...*

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m sec}^{-1}}{7.30 \times 10^{14} \text{ sec}^{-1}} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 411 \text{ nm}$$

OR,

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J sec})(3.00 \times 10^{17} \text{ nm sec}^{-1})}{4.84 \times 10^{-19} \text{ J}} = 411 \text{ nm}$$

1 pt

Note: Point earned for correct wavelength;  $\lambda = 4.11 \times 10^{-7} \text{ m}$  accepted.  
Negative wavelength not accepted.

- (iii) The positive charge holding the electron is greater for  $\text{He}^+$ , which has a 2+ nucleus, than for H with its 1+ nucleus. The stronger attraction means that it requires more energy for the electron to move to higher energy levels. Therefore, transitions from high energy states to lower states will be more energetic for  $\text{He}^+$  than for H.

1 pt

Note: Other arguments accepted, such as, “ $E$  is proportional to  $Z^2$ . Since  $Z = 2$  for  $\text{He}^+$  and  $Z = 1$  for H, all energy levels in  $\text{He}^+$  are raised (by a factor of 4).” Other accepted answers must refer to the increased charge on the  $\text{He}^+$  nucleus, and NOT the mass.

---

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures\* (maximum once per question)

\*number of significant figures must be correct within  $\pm$  one digit

## Scoring Guidelines for Free-Response Question 3

### Question 3

(9 points)

- (a) Rate of  $\text{Br}_2(\text{g})$  loss occurs at  $\frac{1}{2}$  the rate of  $\text{NOBr}(\text{g})$  formation.

$$\text{Rate of } \text{Br}_2(\text{g}) \text{ loss} = \frac{3.24 \times 10^{-4} M}{2 \text{ sec}} = 1.62 \times 10^{-4} M \text{ sec}^{-1} \text{ (or mol L}^{-1} \text{ sec}^{-1}) \quad 1 \text{ pt}$$

Note: No penalty for missing units; ignore + or – signs

- (b) Comparing experiments 1 and 2,  $[\text{NO}]$  remains constant,  $[\text{Br}_2]$  doubles, and rate doubles; therefore,  $\text{rate} \propto [\text{Br}_2]^1 \Rightarrow$  reaction is first-order with respect to  $[\text{Br}_2]$ . 1 pt

$$\frac{6.38 \times 10^{-4}}{6.42 \times 10^{-4}} \cong 1 = \frac{k[\text{NO}]^x[\text{Br}_2]}{k[\text{NO}]^x[\text{Br}_2]} = \frac{k[0.0160]^x[0.0240]}{k[0.0320]^x[0.0060]} = \left(\frac{1}{2}\right)^x 4 = 1 \Rightarrow$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow x = 2 \Rightarrow \text{reaction is second-order with respect to } [\text{NO}] \quad 2 \text{ pts}$$

Note: One point earned for a proper set-up, comparing experiments 2 and 3 (as is shown here) or experiments 1 and 3. Second point earned for solving the ratios correctly and determining that the exponent = 2. Also, credit can be earned for a non-mathematical approach (e.g., one point for describing the change in  $[\text{Br}_2]$  and subsequent effect on rate, another point for describing the change in  $[\text{NO}]$  and subsequent effect on rate).

- (c) (i)  $\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$  1 pt

Note: Point earned for an expression that is not inconsistent with the answer in part (b)

$$(ii) k = \frac{\text{Rate}}{[\text{NO}]^2[\text{Br}_2]} = \frac{3.24 \times 10^{-4} M \text{ sec}^{-1}}{(0.0160)^2(0.0120) M^3} = 105 M^{-2} \text{ sec}^{-1} \text{ (or } 105 \text{ L}^2 \text{ mol}^{-2} \text{ sec}^{-1}) \quad 2 \text{ pts}$$

(Using rate of  $\text{Br}_2(\text{g})$  loss =  $1.62 \times 10^{-4} M \text{ sec}^{-1} \Rightarrow k = 52.7 M^{-2} \text{ sec}^{-1}$  is also correct.)

Note: One point for solving for the value of the rate constant consistent with the rate-law expression found in part (b) or stated in part (c); one point for the correct units consistent with the rate-law expression found in part (b) or stated in part (c).

- (d) No, it is not consistent with the given experimental observations. 1 pt

This mechanism gives a reaction that is first-order in  $[\text{NO}]$ , and first-order in  $[\text{Br}_2]$ , as those are the two reactants in the rate-determining step. Kinetic data show the reaction is second-order in  $[\text{NO}]$  (and first-order in  $[\text{Br}_2]$ ), so this cannot be the mechanism. 1 pt

Note: One point earned for “No” [or for “Yes” if rate =  $k[\text{NO}][\text{Br}_2]$  in part (b)].  
One point earned for justifying why this mechanism is inconsistent with the observed rate-law [or consistent with rate law stated earlier in response].

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One point deduction for mathematical error (maximum once per question)

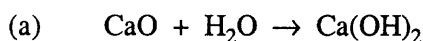
One point deduction for error in significant figures\* (maximum once per question)

\*number of significant figures must be correct within  $\pm$  one digit

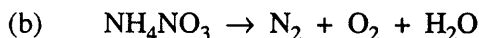
## Scoring Guidelines for Free-Response Question 4

### Question 4 (15 points)

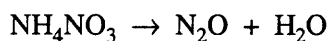
Students choose five of the eight reactions. Only the answers in the boxes are graded (unless clearly marked otherwise). Each correct answer earns 3 points, 1 point for reactants and 2 points for products. All products must be correct to earn both product points. Equations do not need to be balanced and phases need not be indicated. Any spectator ions on the reactant side nullify the 1 possible reactant point, but if they appear again on the product side, there is no product-point penalty. A fully molecular equation (when it should be ionic) earns a maximum of one point. Ion charges must be correct.



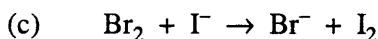
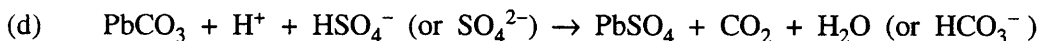
- *No penalty for the set of products  $\{ \text{Ca}^{2+}, \text{OH}^-, \text{and } \text{Ca(OH)}_2 \}$*



OR



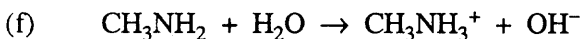
- *Two points earned for  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$*
- *No penalty for other oxides of nitrogen (e.g., NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub> – but not N<sub>2</sub>O<sub>5</sub>)*



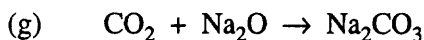
- *No reactant point earned for  $\text{H}_2\text{SO}_4$*
- *No product point earned for  $\text{H}_2\text{CO}_3$*



- *No penalty for the set of products  $\{ \text{FeO}, \text{Fe}, \text{and } \text{Al}_2\text{O}_3 \}$*



- *Two points earned for  $\text{MeNH}_2 + \text{H}_2\text{O} \rightarrow \text{MeNH}_3^+ + \text{OH}^-$*



## Scoring Guidelines for Free-Response Question 5

### Question 5 (8 points)

- (a)  $PV = nRT$  AND  $n = \frac{m}{M}$ , OR  $\text{molar mass} = \frac{mRT}{PV}$ , OR  $M = \frac{DRT}{P}$  1 pt
- (b) temperature, atmospheric pressure, volume of the gas, and mass of gas (mass of pressurized container before and after releasing the gas) 3 pts

Note: 1 point earned for any two of the above, 2 points earned for any three of them.  
 “The mass of the gas” is acceptable as a “measurement” for the 1<sup>st</sup> or 2<sup>nd</sup> point.  
 Extraneous measurements (e.g., density, volume of liquid, etc.) are ignored. To earn 3<sup>rd</sup> point, “mass of pressurized container before and after releasing the gas”, or “change in mass of container” must be indicated.

- (c) to equalize internal pressure with room pressure (atmospheric pressure), or the pressure(s) will be the same. 1 pt
- (d)  $\% \text{ error} = \frac{(64 - 58) \text{ g}}{58 \text{ g}} \times 100\%$  (or  $\frac{6}{58} \times 100\%$ , or  $\frac{6}{58}$ ) 1 pt

Note: No points earned for generic response (e.g.,  $\frac{|\text{expt.} - \text{theor.}|}{\text{theor.}} \times 100$ ),  
 or for  $\frac{6}{64} \times 100\%$ . No penalty if “ $\times 100\%$ ” is absent or if value (10%) is not calculated.

- (e) Pressure will be larger, therefore number of moles will be larger 1 pt  
 $\text{molar mass} = \frac{\text{mass}}{\text{moles}}$ , therefore calculated molar mass will be smaller 1 pt

OR,  $M = \frac{mRT}{PV}$  (or  $M = \frac{DRT}{P}$ ), and the denominator,  $PV$ , will be too large. 2 pts  
 Therefore, the value of the molar mass ( $= \frac{mRT}{PV}$  or  $\frac{DRT}{P}$ ) will be too small.

OR, The pressure is larger, or the number of moles is larger, or since  $P_{\text{total}} = (P_{\text{unknown}} - P_{\text{water}})$  we know that  $P_{\text{total}} > P_{\text{unknown}}$ . 1 pt only

Note: If  $n = \frac{m}{M}$  is missing in part (a) but present in part (e), 1 point is earned for part (a).

## Scoring Guidelines for Free-Response Question 6

### Question 6

(8 points)

- (a) (i)  $\Delta S^\circ$  is negative (–) **OR**  $\Delta S^\circ < 0$  **OR** entropy is decreasing. 1 pt

3 moles of gaseous particles are converted to 2 moles of solid/liquid. 1 pt

- One point earned for correct identification of (–) sign of  $\Delta S^\circ$
- One point earned for correct explanation (mention of phases is crucial for point)
- No point earned if incorrect  $\Delta S^\circ$  sign is obtained from the presumed value of  $\Delta G^\circ$

- (ii)  $\Delta H^\circ$  drives the reaction. 1 pt

The decrease in entropy ( $\Delta S^\circ < 0$ ) cannot drive the reaction, so the decrease in enthalpy ( $\Delta H^\circ < 0$ ) MUST drive the reaction.

**OR**

1 pt

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ; for a spontaneous reaction  $\Delta G^\circ < 0$ , and a negative value of  $\Delta S^\circ$  causes a positive  $\Delta G^\circ$ .

- One point earned for identifying  $\Delta H^\circ$  as the principal driving force for the reaction
- One point earned for correct justification
- Justification point earned by mentioning the effects of changes in entropy and enthalpy on the spontaneity of the reaction **OR** by a mathematical argument using the Gibbs-Helmholtz equation and some implication about the comparison between the effects of  $\Delta S^\circ$  and  $\Delta H^\circ$

- (iii) Given that  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  and  $\Delta S^\circ < 0$ , an increase in temperature causes an increase in the value of  $\Delta G^\circ$  ( $\Delta G^\circ$  becomes less negative). 1 pt

- One point earned for the description of the effect of an increase in temperature on  $\Delta S^\circ$  and consequently on  $\Delta G^\circ$
- No point earned for an argument based on Le Châtelier's principle

- (b) (i) The reaction rate depends on the reaction kinetics, which is determined by the value of the activation energy,  $E_{act}$ . If the activation energy is large, a reaction that is thermodynamically spontaneous may proceed very slowly (if at all). 1 pt

- One point earned for linking the rate of the reaction to the activation energy, which may be explained verbally or shown on a reaction profile diagram

- (ii) The catalyst has no effect on the value of  $\Delta G^\circ$ . 1 pt

The catalyst reduces the value of  $E_{act}$ , increasing the rate of reaction, but has no effect on the values of  $\Delta H^\circ$  and  $\Delta S^\circ$ , so it cannot affect the thermodynamics of the reaction. 1 pt

- One point earned for indicating no change in the value of  $\Delta G^\circ$
- One point earned for indicating (verbally, or with a reaction-profile diagram) that the catalyst affects the activation energy

## Scoring Guidelines for Free-Response Question 7

### Question 7 (8 points)

(a)  $C_2H_5OH$  (Flask #3)

**1 pt**

Ethanol, a nonelectrolyte, does not break up or dissociate in solution.

**1 pt**

- *One point earned for identifying  $C_2H_5OH$*
- *One point earned for the correct explanation.*
- *Explanation point earned for a description of a nonelectrolyte (e.g., something that does not break up or does not dissociate.)*
- *No point earned for describing  $C_2H_5OH$  as organic, or as the compound that contains the most hydrogens.*

(b)  $MgCl_2$  (Flask #2)

**1 pt**

The freezing-point depression is proportional to the concentration of solute particles. All solutes are at the same concentration, but the van't Hoff factor ( $i$ ) is largest for  $MgCl_2$ .

**1 pt**

- *One point earned for identifying  $MgCl_2$ .*
- *One point earned for the correct explanation.*

(c)  $C_2H_5OH$  (Flask #3)

**1 pt**

The lowering of vapor pressure of water is directly proportional to the concentration of solute particles in solution.  $C_2H_5OH$  is the only nonelectrolyte, so it will have the fewest solute particles in solution.

**1 pt**

- *One point earned for identifying  $C_2H_5OH$ .*
- *One point earned for the correct explanation.*

(d)  $NaF$  (Flask #1)

**1 pt**

The  $F^-$  ion, generated upon dissolution of  $NaF$ , is a weak base. It is the only solution with  $pH > 7$ .

**1 pt**

- *One point earned for identifying  $NaF$ .*
- *One point earned for the correct explanation.*

## Scoring Guidelines for Free-Response Question 8

### Question 8

(8 points)

(a) (i)

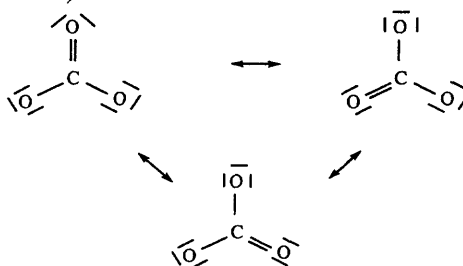
2 pts



- One point earned for each Lewis electron-dot structure
- Indication of lone pairs of electrons are required on each structure
- Resonance forms of  $\text{CO}_3^{2-}$  are not required

(ii) In  $\text{CO}_2$ , the C–O interactions are double bonds, **OR**, in  $\text{CO}_3^{2-}$  the C–O interactions are resonance forms (or figures below.)

1 pt



The carbon-oxygen bond length is greater in the resonance forms than in the double bonds.

1 pt

- 1<sup>st</sup> point earned for indicating double bonds are present in  $\text{CO}_2$  **OR** resonance occurs in  $\text{CO}_3^{2-}$
- 2<sup>nd</sup> point earned for **BOTH** of the above **AND** indicating the relative lengths of the bond types

(b) (i)

2 pts



- One point earned for each Lewis electron-dot structure
- Lone pairs of electrons are required on each structure

(ii)  $\text{CF}_4$  has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule.

1 pt

With five pairs of electrons around the central S atom,  $\text{SF}_4$  exhibits a trigonal bipyramidal electronic geometry, with the lone pair of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar.

1 pt



- One point earned for each molecule for proper geometry and explanation