CHEMISTRY

Section I

Time—1 hour and 30 minutes

NO CALCULATOR 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	L, mL	= liter(s), milliliter(s)
P	= pressure	g	= gram(s)
V	= volume	nm	= nanometer(s)
S	= entropy	atm	= atmosphere(s)
H	= enthalpy	mm Hg	= millimeters of mercury
G	= Gibbs free energy	J, kJ	= joule(s), kilojoule(s)
R	= molar gas constant	V	= volt(s)
n	= number of moles	mol	= mole(s)
M	= molar		
m	= molal		

Part A

Directions: Each set of lettered choices below refers to the numbered statements immediately following it. Select the one that is best in each case and then place the letter of your choice in the corresponding box on the student 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 chemical compounds.

(A) CH_4
(B) CCl_3F
(C) H_2S
(D) H_2O_2
(E) K_2CrO_4

1. Commonly used as a disinfectant for minor skin wounds

2. A refrigerant implicated in the thinning of the stratospheric ozone layer

3. A major component of the fuel known as natural gas

4. A yellow solid at room temperature and 1 atm

Questions 5-7 refer to the following molecules.

(A) CO
(B) CH_4
(C) HF
(D) PH_3
(E) F_2

5. Contains two π-bonds

6. Has the highest dipole moment

7. Has a molecular geometry that is trigonal pyramidal

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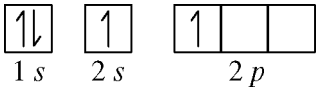
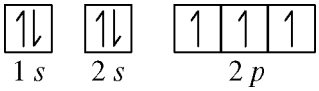
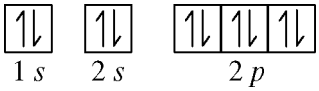
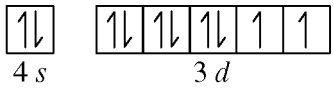
Questions 8-11 refer to neutral atoms for which the atomic orbitals are represented below

(A)

(B) 

(C) 

(D) 

(E) [Ar] 

8. Is in an excited state

9. Has exactly five valence electrons

10. Has the highest first ionization energy

11. Forms an aqueous cation that is colored

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Questions 12-15 refer to the chemical reactions represented below.

(A) $HC_2H_3O_2(aq) + NH_3(aq) \rightarrow C_2H_3O_2^-(aq) + NH_4^+(aq)$

(B) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

(C) $Zn(OH)_2(s) + 2\ OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$

(D) $2\ K(s) + Br_2(l) \rightarrow 2\ KBr(s)$

(E) $N_2O_4(g) \rightarrow 2\ NO_2(g)$

12. An oxidation-reduction reaction

13. A precipitation reaction

14. A reaction in which a coordination complex is formed

15. A Lewis acid-base reaction that is not a Brønsted-Lowry acid-base reaction

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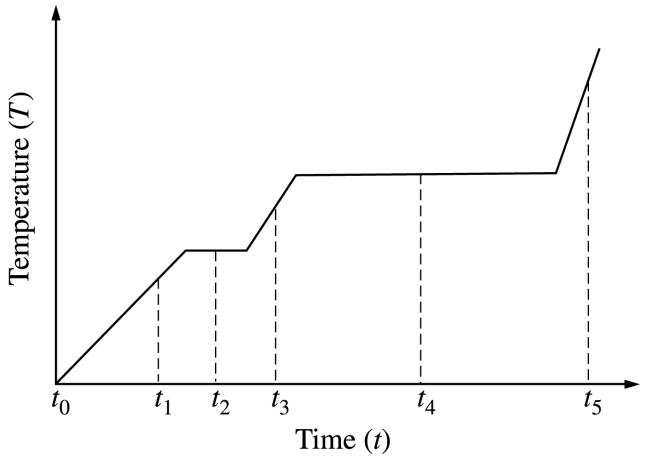
Questions 16-17 refer to various points in time during an experiment conducted at 1.0 atm. Heat is added at a constant rate to a sample of a pure substance that is solid at time t_0. The graph below shows the temperature of the sample as a function of time.



(A) t_1
(B) t_2
(C) t_3
(D) t_4
(E) t_5

16. Time when the average distance between the particles is greatest

17. Time when the temperature of the substance is between its melting point and its boiling point

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 place the letter of your choice in the corresponding box on the student answer sheet.

18. Which of the following is the correct name for the compound with formula Ca_3P_2 ?

    (A) Tricalcium diphosphorus
    (B) Calcium phosphite
    (C) Calcium phosphate
    (D) Calcium diphosphate
    (E) Calcium phosphide

19. What mass of KBr (molar mass 119 g mol^{-1}) is required to make 250. mL of a 0.400 *M* KBr solution?

    (A) 0.595 g
    (B) 1.19 g
    (C) 2.50 g
    (D) 11.9 g
    (E) 47.6 g

20. The value of the acid-dissociation constant, K_a, for a weak monoprotic acid HA is 2.5×10^{-6}. The pH of 0.40 *M* HA is closest to

    (A) 2.0
    (B) 3.0
    (C) 4.0
    (D) 6.0
    (E) 8.0

21. Which of the systems in equilibrium represented below will exhibit a shift to the left (toward reactants) when the pressure on the system is increased by reducing the volume of the system? (Assume that temperature is constant.)

    (A) $2\ Mg(s) + O_2(g) \rightleftarrows 2\ MgO(s)$
    (B) $SF_4(g) + F_2(g) \rightleftarrows SF_6(g)$
    (C) $H_2(g) + Br_2(g) \rightleftarrows 2\ HBr(g)$
    (D) $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$
    (E) $SO_2Cl_2(g) \rightleftarrows SO_2(g) + Cl_2(g)$

22. The standard enthalpy of formation, ΔH_f°, of $HI(g)$ is +26 kJ mol^{-1}. Which of the following is the approximate mass of $HI(g)$ that must decompose into $H_2(g)$ and $I_2(s)$ to release 500. kJ of energy?

    (A) 250 g
    (B) 650 g
    (C) 1,300 g
    (D) 2,500 g
    (E) 13,000 g

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$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$$

23. For the process of solid calcium chloride dissolving in water, represented above, the entropy change might be expected to be positive. However, ΔS for the process is actually negative. Which of the following best helps to account for the net loss of entropy?

(A) Cl^- ions are much larger in size than Ca^{2+} ions.
(B) The particles in solid calcium chloride are more ordered than are particles in amorphous solids.
(C) Water molecules in the hydration shells of Ca^{2+} and Cl^- ions are more ordered than they are in the pure water.
(D) The $Ca^{2+}(aq)$ and $Cl^-(aq)$ ions are more free to move around in solution than they are in $CaCl_2(s)$.
(E) In the solution, the average distance between $Ca^{2+}(aq)$ and $Cl^-(aq)$ is greater than the average distance between Ca^{2+} and Cl^- in $CaCl_2(s)$.

$$\ldots CH_3OCH_3(g) + \ldots O_2(g) \rightarrow \ldots CO_2(g) + \ldots H_2O(g)$$

24. When the equation above is balanced using the lowest whole-number coefficients, the coefficient for $O_2(g)$ is

(A) 6
(B) 4
(C) 3
(D) 2
(E) 1

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25. For which of the following processes does entropy decrease ($\Delta S < 0$) ?

(A) $H_2O(s) \rightarrow H_2O(l)$
(B) $Br_2(l) \rightarrow Br_2(g)$
(C) Crystallization of $I_2(s)$ from an ethanol solution
(D) Thermal expansion of a balloon filled with $CO_2(g)$
(E) Mixing of equal volumes of $H_2O(l)$ and $CH_3OH(l)$

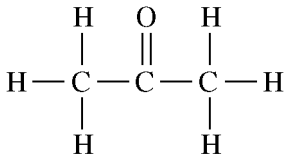
26. In a laboratory, a student wants to quantitatively collect the CO_2 gas generated by adding $Na_2CO_3(s)$ to 2.5 *M* HCl. The student sets up the apparatus to collect the CO_2 gas over water. The volume of collected gas is much less than the expected volume because CO_2 gas

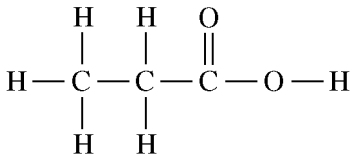
(A) is very soluble in water
(B) is produced at a low pressure
(C) is more dense than water vapor
(D) has a larger molar mass than that of N_2 gas, the major component of air
(E) has a slower average molecular speed than water vapor at the same temperature

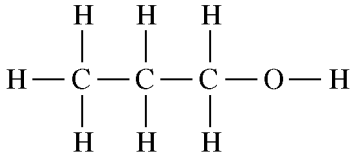
27. What mass of $Cu(s)$ would be produced if 0.40 mol of $Cu_2O(s)$ was reduced completely with excess $H_2(g)$?

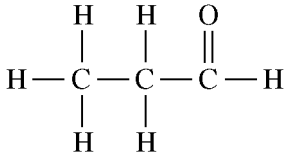
(A) 13 g
(B) 25 g
(C) 38 g
(D) 51 g
(E) 100 g

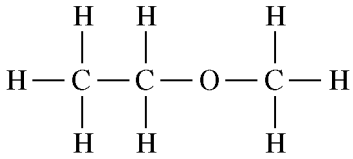
28. Which of the following is a formula for an ether?

(A) 

(B) 

(C) 

(D) 

(E) 

Gas	Amount
Ar	0.35 mol
CH_4	0.90 mol
N_2	0.25 mol

29. Three gases in the amounts shown in the table above are added to a previously evacuated rigid tank. If the total pressure in the tank is 3.0 atm at 25°C, the partial pressure of $N_2(g)$ in the tank is closest to

(A) 0.75 atm
(B) 0.50 atm
(C) 0.33 atm
(D) 0.25 atm
(E) 0.17 atm

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30. Which of the following best explains why the normal boiling point of $CCl_4(l)$ (350 K) is higher than the normal boiling point of $CF_4(l)$ (145 K) ?

(A) The C–Cl bonds in CCl_4 are less polar than the C–F bonds in CF_4.

(B) The C–Cl bonds in CCl_4 are weaker than the C–F bonds in CF_4.

(C) The mass of the CCl_4 molecule is greater than that of the CF_4 molecule.

(D) The electron cloud of the CCl_4 molecule is more polarizable than that of the CF_4 molecule.

(E) The bonds in the CCl_4 molecule are covalent, whereas the bonds in the CF_4 molecule are ionic.

31. At which of the following temperatures and pressures would a real gas be most likely to deviate from ideal behavior?

	Temperature (K)	Pressure (atm)
(A)	100	50
(B)	200	5
(C)	300	0.01
(D)	500	0.01
(E)	500	1

32. After 195 days, a 10.0 g sample of pure ^{95}Zr has decayed to the extent that only 1.25 g of the original ^{95}Zr remains. The half-life of ^{95}Zr is closest to

(A) 195 days
(B) 97.5 days
(C) 65.0 days
(D) 48.8 days
(E) 24.4 days

33. Which of the following would produce the LEAST mass of CO_2 if completely burned in excess oxygen gas?

(A) 10.0 g CH_4
(B) 10.0 g CH_3OH
(C) 10.0 g C_2H_4
(D) 10.0 g C_2H_6
(E) 10.0 g C_4H_5OH

34. Which of the following substances exhibits significant hydrogen bonding in the liquid state?

(A) CH_2F_2
(B) N_2H_4
(C) CH_3OCH_3
(D) C_2H_4
(E) C_2H_2

35. In an aqueous solution with a pH of 11.50 at 25°C, the molar concentration of $OH^-(aq)$ is approximately

(A) $3.2 \times 10^{-12}\ M$
(B) $3.2 \times 10^{-3}\ M$
(C) $2.5 \times 10^{-1}\ M$
(D) $2.5\ M$
(E) $3.2 \times 10^{11}\ M$

36. Which of the following changes to a reaction system in equilibrium would affect the value of the equilibrium constant, K_{eq}, for the reaction? (Assume in each case that all other conditions are held constant.)

(A) Adding more of the reactants to the system
(B) Adding a catalyst for the reaction to the system
(C) Increasing the temperature of the system
(D) Increasing the pressure on the system
(E) Removing some of the reaction products from the system

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Questions 37-38 refer to a galvanic cell constructed using two half-cells and based on the two half-reactions represented below.

$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$ $\quad E° = -0.76$ V
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $\quad E° = 0.77$ V

37. As the cell operates, ionic species that are found in the half-cell containing the cathode include which of the following?

I. $Zn^{2+}(aq)$
II. $Fe^{2+}(aq)$
III. $Fe^{3+}(aq)$

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

38. What is the standard cell potential for the galvanic cell?

(A) −0.01 V
(B) 0.01 V
(C) 0.78 V
(D) 1.53 V
(E) 2.31 V

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Ionization Energies for Element X

	1st	2nd	3rd	4th	5th	6th	7th
Ionization Energy ($kJ\ mol^{-1}$)	787	1,580	3,200	4,400	16,000	20,000	24,000

39. The first seven ionization energies of element X are shown in the table above. On the basis of these data, element X is most likely a member of which of the following groups (families) of elements?

(A) Alkaline earth metals
(B) Boron group
(C) Carbon group
(D) Nitrogen group
(E) Halogen group

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40. Which of the following particles is emitted by an atom of ^{39}Ca when it decays to produce an atom of ^{39}K ?

(A) $^{4}_{2}He$
(B) $^{1}_{0}n$
(C) $^{1}_{1}H$
(D) β^{-}
(E) β^{+}

41. At approximately what temperature will 40. g of argon gas at 2.0 atm occupy a volume of 22.4 L?

(A) 1,200 K
(B) 600 K
(C) 550 K
(D) 270 K
(E) 140 K

42. Which of the following aqueous solutions has the highest boiling point at 1.0 atm?

(A) 0.20 *M* $CaCl_2$
(B) 0.25 *M* Na_2SO_4
(C) 0.30 *M* NaCl
(D) 0.30 *M* KBr
(E) 0.40 *M* $C_6H_{12}O_6$

43. A certain reaction is spontaneous at temperatures below 400. K but is not spontaneous at temperatures above 400. K. If $\Delta H°$ for the reaction is $-20.\ kJ\ mol^{-1}$ and it is assumed that $\Delta H°$ and $\Delta S°$ do not change appreciably with temperature, then the value of $\Delta S°$ for the reaction is

(A) $-50.\ J\ mol^{-1}\ K^{-1}$
(B) $-20.\ J\ mol^{-1}\ K^{-1}$
(C) $-0.050\ J\ mol^{-1}\ K^{-1}$
(D) $20.\ J\ mol^{-1}\ K^{-1}$
(E) $8{,}000\ J\ mol^{-1}\ K^{-1}$

44. A sample of a solution of RbCl (molar mass $121\ g\ mol^{-1}$) contains 11.0 percent RbCl by mass. From the following information, what is needed to determine the molarity of RbCl in the solution?

I. Mass of the sample
II. Volume of the sample
III. Temperature of the sample

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

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$$\ldots Au^{3+}(aq) + \ldots I^{-}(aq) \rightarrow \ldots Au(s) + \ldots I_2(s)$$

45. When the equation above is balanced using the lowest whole-number coefficients, the coefficient for $I_2(s)$ is

(A) 8
(B) 6
(C) 4
(D) 3
(E) 2

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46. A closed rigid container contains distilled water and $N_2(g)$ at equilibrium. Actions that would increase the concentration of $N_2(g)$ in the water include which of the following?

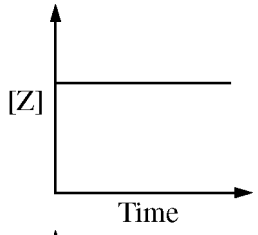
I. Shaking the container vigorously
II. Raising the temperature of the water
III. Injecting more $N_2(g)$ into the container

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

$$Z \rightarrow X + Y$$

47. A pure substance Z decomposes into two products, X and Y, as shown by the equation above. Which of the following graphs of the concentration of Z versus time is consistent with the rate of the reaction being first order with respect to Z ?

(A)



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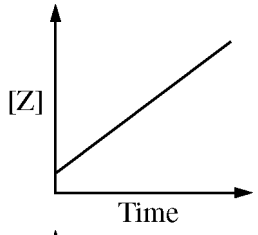

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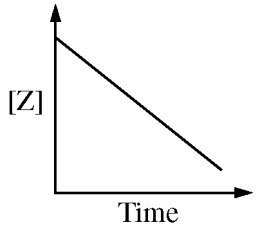

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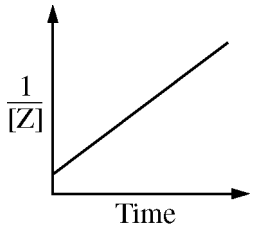
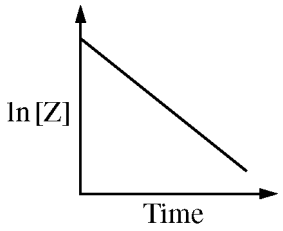


(E)



$$CS_2(l) + 3\ O_2(g) \rightarrow CO_2(g) + 2\ SO_2(g)$$

48. When 0.60 mol of $CS_2(l)$ reacts as completely as possible with 1.5 mol of $O_2(g)$ according to the equation above, the total number of moles of reaction products is

(A) 2.4 mol
(B) 2.1 mol
(C) 1.8 mol
(D) 1.5 mol
(E) 0.75 mol

Questions 49-50 refer to an experiment to determine the value of the heat of fusion of ice. A student used a calorimeter consisting of a polystyrene cup and a thermometer. The cup was weighed, then filled halfway with warm water, then weighed again. The temperature of the water was measured, and some ice cubes from a 0°C ice bath were added to the cup. The mixture was gently stirred as the ice melted, and the lowest temperature reached by the water in the cup was recorded. The cup and its contents were weighed again.

49. The purpose of weighing the cup and its contents again at the end of the experiment was to

(A) determine the mass of ice that was added
(B) determine the mass of the thermometer
(C) determine the mass of water that evaporated
(D) verify the mass of water that was cooled
(E) verify the mass of the calorimeter cup

50. Suppose that during the experiment, a significant amount of water from the ice bath adhered to the ice cubes. How does this affect the calculated value for the heat of fusion of ice?

(A) The calculated value is too large because less warm water had to be cooled.
(B) The calculated value is too large because more cold water had to be heated.
(C) The calculated value is too small because less ice was added than the student assumed.
(D) The calculated value is too small because the total mass of the calorimeter contents was too large.
(E) There is no effect on the calculated value because the water adhered to the ice cubes was at 0°C.

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51. Which of the following molecules contains bonds that have a bond order of 1.5 ?

(A) N_2
(B) O_3
(C) NH_3
(D) CO_2
(E) CH_2CH_2

52. Of the following metals, which reacts violently with water at 298 K?

(A) Au
(B) Ag
(C) Cu
(D) Mg
(E) Rb

53. Heat energy is added slowly to a pure solid covalent compound at its melting point. About half of the solid melts to become a liquid. Which of the following must be true about this process?

(A) Covalent bonds are broken as the solid melts.
(B) The temperature of the solid/liquid mixture remains the same while heat is being added.
(C) The intermolecular forces present among molecules become zero as the solid melts.
(D) The volume of the compound increases as the solid melts to become a liquid.
(E) The average kinetic energy of the molecules becomes greater as the molecules leave the solid state and enter the liquid state.

54. A steady electric current is passed through molten $MgCl_2$ for exactly 1.00 hour, producing 243 g of Mg metal. If the same current is passed through molten $AlCl_3$ for 1.00 hour, the mass of Al metal produced is closest to

(A) 27.0 g
(B) 54.0 g
(C) 120. g
(D) 180. g
(E) 270. g

$$F^-(aq) + H_2O(l) \rightleftarrows HF(aq) + OH^-(aq)$$

55. Which of the following species, if any, acts as a Brønsted-Lowry base in the reversible reaction represented above?

(A) HF(*aq*)
(B) $H_2O(l)$
(C) $F^-(aq)$ only
(D) Both $F^-(aq)$ and $OH^-(aq)$ act as Brønsted-Lowry bases.
(E) No species acts as a Brønsted-Lowry base.

56. What is the empirical formula of a hydrocarbon that is 10.0 percent hydrogen by mass?

(A) CH_3
(B) C_2H_5
(C) C_3H_4
(D) C_4H_9
(E) C_9H_{10}

$$Pb(s) \rightleftarrows Pb(l)$$

57. Which of the following is true for the process represented above at 327°C and 1 atm? (The normal melting point of Pb(*s*) is 327°C.)

(A) $\Delta H = 0$
(B) $T\Delta S = 0$
(C) $\Delta S < 0$
(D) $\Delta H = T\Delta G$
(E) $\Delta H = T\Delta S$

GO ON TO THE NEXT PAGE.

$$N_2(g) + O_2(g) + Cl_2(g) \rightleftarrows 2\ NOCl(g) \qquad \Delta H^\circ = +104\ kJ\ mol^{-1}$$

58. The equilibrium system represented above is contained in a sealed, rigid vessel. Which of the following will <u>increase</u> if the temperature of the mixture is raised?

(A) $[N_2(g)]$
(B) The rate of the forward reaction only
(C) The rate of the reverse reaction only
(D) The rates of both the forward and reverse reactions
(E) The total number of moles of gas in the vessel

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59. If a metal X forms an ionic chloride with the formula XCl_3, then which of the following formulas is most likely to be that of a stable sulfide of X?

(A) XS_2
(B) X_2S_3
(C) XS_6
(D) $X(SO_3)_3$
(E) $X_2(SO_3)_3$

Questions 60-61 refer to the figures below. The figures show portions of a buret used in a titration of an acid solution of known concentration with a saturated solution of $Ba(OH)_2$. Figures 1 and 2 show the level of the $Ba(OH)_2$ solution at the start and at the endpoint of the titration, respectively. Phenolphthalein was used as the indicator for the titration.

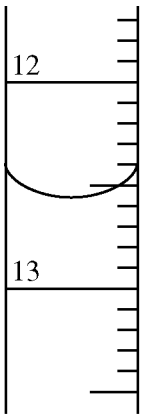


Figure 1

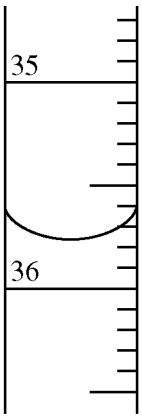


Figure 2

60. What is the evidence that the endpoint of the titration has been reached?

(A) The color of the solution in the buret changes from pink to colorless.
(B) The color of the solution in the buret changes from blue to red.
(C) The color of the contents of the flask below the buret changes from colorless to pink.
(D) The color of the contents of the flask below the buret changes from blue to red.
(E) The contents of the flask below the buret change from clear to cloudy.

61. The volume of saturated $Ba(OH)_2$ used to neutralize the acid was closest to

(A) 6.60 mL
(B) 22.80 mL
(C) 23.02 mL
(D) 23.20 mL
(E) 29.80 mL

GO ON TO THE NEXT PAGE.

$$C(\text{diamond}) \rightarrow C(\text{graphite})$$

62. For the reaction represented above, the standard Gibbs free energy change, ΔG°_{298}, has a value of -2.90 kJ mol^{-1}. Which of the following best accounts for the observation that the reaction does NOT occur (i.e., diamond is stable) at 298 K and 1.00 atm?

(A) ΔS° for the reaction is positive.
(B) The activation energy, E_a, for the reaction is very large.
(C) The reaction is slightly exothermic ($\Delta H^{\circ} < 0$).
(D) Diamond has a density greater than that of graphite.
(E) Diamond has a heat capacity lower than that of graphite.

$$8\ H_2(g) + S_8(s) \rightarrow 8\ H_2S(g)$$

63. When 25.6 g of $S_8(s)$ (molar mass 256 g mol^{-1}) reacts completely with an excess of $H_2(g)$ according to the equation above, the volume of $H_2S(g)$, measured at 0°C and 1.00 atm, produced is closest to

(A) 30 L
(B) 20 L
(C) 10 L
(D) 5 L
(E) 2 L

$$2\ HClO + 3\ O_2 \rightarrow 2\ HClO_4$$

64. As the reaction represented above proceeds to the right, the oxidation number of chlorine changes from

(A) −1 to +3
(B) −1 to +5
(C) +1 to +5
(D) +1 to +7
(E) +3 to +7

65. By mixing only 0.15 *M* HCl and 0.25 *M* HCl, it is possible to create all of the following solutions EXCEPT

(A) 0.23 *M* HCl
(B) 0.21 *M* HCl
(C) 0.18 *M* HCl
(D) 0.16 *M* HCl
(E) 0.14 *M* HCl

66. At 25°C a saturated solution of a metal hydroxide, $M(OH)_2$, has a pH of 9.0. What is the value of the solubility-product constant, K_{sp}, of $M(OH)_2(s)$ at 25°C?

(A) 5.0×10^{-28}
(B) 1.0×10^{-27}
(C) 5.0×10^{-19}
(D) 5.0×10^{-16}
(E) 1.0×10^{-15}

GO ON TO THE NEXT PAGE.

67. A student weighs out 0.0154 mol of pure, dry NaCl in order to prepare a 0.154 *M* NaCl solution. Of the following pieces of laboratory equipment, which would be most essential for preparing the solution?

(A) Large crucible with lid
(B) 50 mL volumetric pipet
(C) 100 mL Erlenmeyer flask
(D) 100 mL graduated beaker
(E) 100 mL volumetric flask

68. In which of the following are the chemical species correctly ordered from smallest radius to largest radius?

(A) B < C < N
(B) Ar < Xe < Kr
(C) Cl < S < S^{2-}
(D) Na < Na^{+} < K
(E) K^{+} < Ca^{2+} < K

69. A large piece of wood can burn slowly, but wood in the form of sawdust can combust explosively. The primary reason for the difference is that compared with a large piece of wood, sawdust

(A) has a greater surface area per kilogram
(B) has a greater carbon content per kilogram
(C) absorbs more atmospheric moisture per kilogram
(D) contains more compounds that act as catalysts for combustion
(E) contains more compounds that have higher heats of combustion

70. Of the following elements, which would be expected to have chemical properties most similar to those of sulfur, S ?

(A) Br
(B) Cl
(C) N
(D) P
(E) Se

71. When a solution is formed by adding some methanol, CH_3OH, to water, processes that are endothermic include which of the following?

I. Methanol molecules move water molecules apart as the methanol goes into solution.
II. Water molecules move methanol molecules apart as the methanol goes into solution.
III. Intermolecular attractions form between molecules of water and methanol as the methanol goes into solution.

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

72. Of the following gases, which has the greatest average molecular speed at 298 K?

(A) $Cl_2(g)$
(B) NO(g)
(C) $H_2S(g)$
(D) HCN(g)
(E) $PH_3(g)$

73. Types of hybridization exhibited by carbon atoms in a molecule of propyne, CH_3CCH, include which of the following?

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

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

GO ON TO THE NEXT PAGE.

$$XY_2(aq) \rightleftarrows X^{2+}(aq) + 2\ Y^{-}(aq)$$

74. A soluble compound XY_2 dissociates in water according to the equation above. In a 0.050 *m* solution of the compound, the $XY_2(aq)$ species is 40.0 percent dissociated. In the solution, the number of moles of particles of solute per 1.0 kg of water is closest to

(A) 0.15
(B) 0.090
(C) 0.070
(D) 0.040
(E) 0.020

75. In which of the following processes are covalent bonds broken?

(A) Solid silver melts.
(B) Solid potassium chloride melts.
(C) Solid carbon (graphite) sublimes.
(D) Solid iodine sublimes.
(E) Glucose dissolves in water.

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—95 minutes)

Part A

Time—55 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since 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.

1. Answer the following questions about the solubility of the salts Li_3PO_4 and $PbCl_2$. Assume that hydrolysis effects are negligible.

   The equation for the dissolution of $Li_3PO_4(s)$ is shown below.

   $$Li_3PO_4(s) \rightleftarrows 3\ Li^+(aq) + PO_4^{3-}(aq) \qquad K_{sp} = 3.2 \times 10^{-9} \text{ at } 25°C$$

   (a) Write the equilibrium-constant expression for the dissolution of $Li_3PO_4(s)$.

   (b) Assuming that volume changes are negligible, calculate the maximum number of moles of $Li_3PO_4(s)$ that can dissolve in

   (i) 0.50 L of water at 25°C

   (ii) 0.50 L of 0.20 *M* $LiNO_3$ at 25°C

   The equation for the dissolution of $PbCl_2$ is shown below.

   $$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ Cl^-(aq) \qquad K_{sp} = 1.6 \times 10^{-5} \text{ at } 25°C$$

   (c) Calculate the concentration of $Cl^-(aq)$ in a saturated solution of $PbCl_2$ at 25°C.

   (d) An open container holds 1.000 L of 0.00400 *M* $PbCl_2$, which is unsaturated at 25°C. Calculate the minimum volume of water, in mL, that must evaporate from the container before solid $PbCl_2$ can precipitate.

GO ON TO THE NEXT PAGE.

2. Answer the following using chemical concepts and principles of the behavior of gases.

(a) A metal cylinder with a volume of 5.25 L contains 3.22 g of $He(g)$ and 11.56 g of $N_2(g)$ at 15.0°C.

(i) Calculate the total pressure in the cylinder.

(ii) Calculate the partial pressure of $N_2(g)$ in the cylinder.

(b) A 1.50 L container holds a 9.62 g sample of an unknown gaseous saturated hydrocarbon at 30°C and 3.62 atm.

(i) Calculate the density of the gas.

(ii) Calculate the molar mass of the gas.

(iii) Write the formula of the hydrocarbon.

(iv) Calculate the root-mean-square speed of the gas molecules in the container at 30°C.
(Note: 1 J = 1 kg m^2 s^{-2})

---

3. A student performs a titration in which a 10.00 mL sample of 0.0571 *M* HCl is titrated with a solution of NaOH of unknown concentration.

(a) Describe the steps that the student should take to prepare and fill the buret for the titration given a wet 50.00 mL buret and the materials listed below.

0.0571 *M* HCl solution	Indicator solution
NaOH(*aq*) (unknown concentration)	Distilled water
10.5 *M* NaOH solution	100 mL beaker

(b) Calculate the pH of the 0.0571 *M* HCl.

(c) A volume of 7.62 mL of the NaOH solution was needed to reach the end point of the titration. Calculate the molarity of the NaOH solution used in the titration.

In a different titration using a different NaOH solution, the concentration of NaOH was determined by the student to be 0.0614 *M*.

(d) Given that the actual concentration of the NaOH solution was 0.0627 *M*, calculate the percent error of the student's result.

(e) Calculate the volume of 10.5 *M* NaOH that is needed to prepare 250.0 mL of 0.0627 *M* NaOH.

S T O P

If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.

CHEMISTRY

Part B

Time—40 minutes

NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 10 percent.

4. For each of the following three reactions, in part (i) write a balanced equation and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be graded.

EXAMPLE:

A strip of magnesium metal is added to a solution of silver(I) nitrate.

(i) Balanced equation:

$$Mg + 2\,Ag^{+} \longrightarrow Mg^{2+} + 2\,Ag$$

(ii) Which substance is oxidized in the reaction?

Mg is oxidized.

(a) Equal volumes of 0.1 *M* hydrofluoric acid and 0.1 *M* potassium hydroxide are combined.

(i) Balanced equation:

(ii) Draw the complete Lewis electron-dot diagram for the reactant that is the Brønsted-Lowry base in the forward reaction.

GO ON TO THE NEXT PAGE.

(b) Solid calcium metal burns in air.

(i) Balanced equation:

(ii) Predict the algebraic sign of $\Delta H°$ for the reaction. Explain your prediction.

_____

_____

(c) Samples of nitrogen monoxide gas and oxygen gas are combined.

(i) Balanced equation:

(ii) If the reaction is second order with respect to nitrogen monoxide and first order with respect to oxygen, what is the rate law for the reaction?

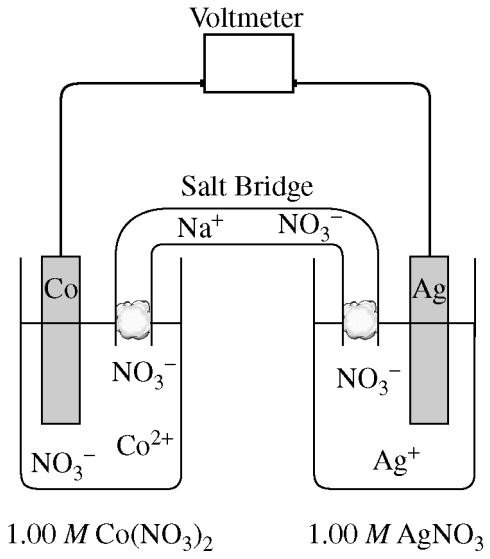
_____

_____

GO ON TO THE NEXT PAGE.

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions 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.



5. Answer the following questions relating to the galvanic cell shown in the diagram above.

   (a) Write the balanced equation for the overall cell reaction.

   (b) Calculate the value of $E°$ for the cell.

   (c) Is the value of $\Delta G°$ for the overall cell reaction positive, negative, or 0 ? Justify your answer.

   (d) Consider the cell as it is operating.

      (i) Does E_{cell} increase, decrease, or remain the same? Explain.

      (ii) Does ΔG of the overall cell reaction increase, decrease, or remain the same? Explain.

      (iii) What would happen if the $NaNO_3$ solution in the salt bridge was replaced with distilled water? Explain.

   (e) After a certain amount of time, the mass of the Ag electrode changes by x grams. Given that the molar mass of Ag is 108 g mol^{-1} and the molar mass of Co is 59 g mol^{-1}, write the expression for the change in the mass of the Co electrode in terms of x.

GO ON TO THE NEXT PAGE.

6. Answer each of the following using principles of atomic or molecular structure, and/or intermolecular or intramolecular forces.

(a) Explain why the H–O–H bond angle in H_2O is less than the H–N–H bond angles in NH_3, as shown in the table below.

H–O–H Bond Angle in H_2O	H–N–H Bond Angles in NH_3
104.5°	107°

(b) Explain why the radius of the Br atom is less than the radius of the Br^- ion, as shown in the table below.

Radius of Br	Radius of Br^-
0.111 nm	0.196 nm

(c) Explain why the dipole moment of HI is less than the dipole moment of HCl, as shown in the table below.

Dipole Moment of HI	Dipole Moment of HCl
0.42 debye	1.08 debyes

(d) Explain why the normal boiling point of Ne is less than the normal boiling point of Kr, as shown in the table below.

Normal Boiling Point of Ne	Normal Boiling Point of Kr
27 K	121 K

STOP

END OF EXAM

**IF YOU FINISH PART B OF SECTION II BEFORE TIME IS CALLED,
YOU MAY RETURN TO PART A OF SECTION II IF YOU WISH,
BUT YOU MAY NOT USE A CALCULATOR.**

INFORMATION IN THE TABLE BELOW AND IN THE TABLES ON PAGES 23-25 MAY BE USEFUL IN ANSWERING THE QUESTIONS IN THIS SECTION OF THE EXAMINATION.

PERIODIC TABLE OF THE ELEMENTS

1																	2
H																	**He**
1.008																	4.00
3	4											5	6	7	8	9	10
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
6.94	9.01											10.81	12.01	14.01	16.00	19.00	20.18
11	12											13	14	15	16	17	18
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
22.99	24.30											26.98	28.09	30.97	32.06	35.45	39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
39.10	40.08	44.96	47.90	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.39	69.72	72.59	74.92	78.96	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
85.47	87.62	88.91	91.22	92.91	95.94	(98)	101.1	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.91	131.29
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	**Ba**	***La**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
132.91	137.33	138.91	178.49	180.95	183.85	186.21	190.2	192.2	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111							
Fr	**Ra**	**†Ac**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**							
(223)	226.02	227.03	(261)	(262)	(266)	(264)	(277)	(268)	(271)	(272)							

	58	59	60	61	62	63	64	65	66	67	68	69	70	71
*Lanthanide Series	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	140.12	140.91	144.24	(145)	150.4	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
	90	91	92	93	94	95	96	97	98	99	100	101	102	103
†Actinide Series	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)

GO ON TO THE NEXT PAGE.

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$F_2(g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Cl_2(g) + 2e^-$	→	$2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	→	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2(s) + 2e^-$	→	$2I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$S(s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→	$Pb(s)$	−0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	−0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	−0.25
$Co^{2+} + 2e^-$	→	$Co(s)$	−0.28
$Cd^{2+} + 2e^-$	→	$Cd(s)$	−0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	−0.41
$Fe^{2+} + 2e^-$	→	$Fe(s)$	−0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	−0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	→	$H_2(g) + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	→	$Mn(s)$	−1.18
$Al^{3+} + 3e^-$	→	$Al(s)$	−1.66
$Be^{2+} + 2e^-$	→	$Be(s)$	−1.70
$Mg^{2+} + 2e^-$	→	$Mg(s)$	−2.37
$Na^+ + e^-$	→	$Na(s)$	−2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	−2.87
$Sr^{2+} + 2e^-$	→	$Sr(s)$	−2.89
$Ba^{2+} + 2e^-$	→	$Ba(s)$	−2.90
$Rb^+ + e^-$	→	$Rb(s)$	−2.92
$K^+ + e^-$	→	$K(s)$	−2.92
$Cs^+ + e^-$	→	$Cs(s)$	−2.92
$Li^+ + e^-$	→	$Li(s)$	−3.05

GO ON TO THE NEXT PAGE.

ATOMIC STRUCTURE

$$E = h\nu \qquad c = \lambda\nu$$

$$\lambda = \frac{h}{m\upsilon} \qquad p = m\upsilon$$

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

EQUILIBRIUM

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

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

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

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

$$14 = pH + pOH$$

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

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

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

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

where Δn = moles product gas − moles reactant gas

THERMOCHEMISTRY/KINETICS

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

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

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT\ln K = -2.303RT\log K$$
$$= -n\mathcal{F}E^\circ$$

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

$$q = mc\Delta T$$

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

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

E = energy
υ = velocity
ν = frequency
n = principal quantum number
λ = wavelength
m = mass
p = momentum

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

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

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

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

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

1 electron volt per atom = 96.5 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° = standard entropy
H° = standard enthalpy
G° = standard free energy
E° = standard reduction potential
T = temperature
n = moles
m = mass
q = heat
c = specific heat capacity
C_p = molar heat capacity at constant pressure
E_a = activation energy
k = rate constant
A = frequency factor

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

Gas constant, R = 8.31 J mol^{-1} K^{-1}
= 0.0821 L atm mol^{-1} K^{-1}
= 62.4 L torr mol^{-1} K^{-1}
= 8.31 volt coulomb mol^{-1} K^{-1}

GO ON TO THE NEXT PAGE.

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

$$P_{total} = P_A + P_B + P_C + \ldots$$

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

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

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

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

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

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

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

$$\frac{r_1}{r_2} = \sqrt{\frac{\boldsymbol{M}_2}{\boldsymbol{M}_1}}$$

molarity, M = moles solute per liter solution

molality = moles solute per kilogram solvent

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

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

$$\pi = iMRT$$

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
D = density
m = mass
υ = velocity

u_{rms} = root-mean-square speed
KE = kinetic energy
r = rate of effusion
$\boldsymbol{M}$ = molar mass
π = osmotic pressure
i = van't Hoff factor
K_f = molal freezing-point depression constant
K_b = molal boiling-point elevation constant
A = absorbance
a = molar absorptivity
b = path length
c = concentration
Q = reaction quotient
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
E° = standard reduction potential
K = equilibrium constant

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

Gas constant, R = 8.31 J mol^{-1} K^{-1}
= 0.0821 L atm mol^{-1} K^{-1}
= 62.4 L torr mol^{-1} K^{-1}
= 8.31 volt coulomb mol^{-1} K^{-1}

Boltzmann's constant, k = 1.38×10^{-23} J K^{-1}

K_f for H_2O = 1.86 K kg mol^{-1}

K_b for H_2O = 0.512 K kg mol^{-1}

1 atm = 760 mm Hg
= 760 torr

STP = 0.00 °C and 1.0 atm

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

GO ON TO THE NEXT PAGE.

APPENDIX - ANSWERS

AP CHEMISTRY 2009

Multiple-choice key transcribed from the matching supplied source.

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

Matching original FRQ scoring material follows in this appendix.

General Scoring Principles

In regard to mathematical errors, a 1-point deduction is made; this deduction may be applied only once per question. In regard to errors in reporting significant figures, a 1-point deduction is made; this deduction may be applied only once per question. A leeway of plus or minus one significant figure different from the correct number of significant figures is allowed before a 1-point deduction is made.

For questions including parts that refer back to previous parts of the same question, a wrong answer that derives from the correct use of a previously calculated incorrect answer should not be counted as wrong. The emphasis of scoring is on *process*, and an error made early on in a multipart calculation should not jeopardize the earning of full credit for the correct use of that incorrect value later in the same question.

Question 1

Answer the following questions about the solubility of the salts Li_3PO_4 and $PbCl_2$. Assume that hydrolysis effects are negligible.

The equation for the dissolution of $Li_3PO_4(s)$ is shown below.

$$Li_3PO_4(s) \rightleftarrows 3\,Li^+(aq) + PO_4^{3-}(aq) \qquad K_{sp} = 3.2 \times 10^{-9} \text{ at } 25°C$$

(a) Write the equilibrium-constant expression for the dissolution of $Li_3PO_4(s)$.

$K_{sp} = [Li^+]^3[PO_4^{3-}]$	One point is earned for the correct expression.

(b) Assuming that volume changes are negligible, calculate the maximum number of moles of $Li_3PO_4(s)$ that can dissolve in

(i) 0.50 L of water at 25°C

Let x represent the molar concentration of Li_3PO_4 present in a saturated solution of Li_3PO_4. Then $K_{sp} = 3.2 \times 10^{-9} = (3x)^3(x) = 27x^4$, thus $x = \sqrt[4]{\frac{3.2 \times 10^{-9}}{27}} = 3.3 \times 10^{-3}\,M$. Therefore the number of moles of $Li_3PO_4(s)$ that can dissolve in 0.50 L of water is $0.50 \text{ L} \times \frac{3.3 \times 10^{-3} \text{ mol } Li_3PO_4}{1.0 \text{ L}} = \mathbf{1.7 \times 10^{-3} \text{ mol}}$	One point is earned for a correct setup using the K_{sp} expression from part (a). One point is earned for a correct calculation of moles of Li_3PO_4.

(ii) 0.50 L of 0.20 M $LiNO_3$ at 25°C

In 0.20 M $LiNO_3$, $[Li^+] = 0.20\,M$. Assume that the amount of $Li^+(aq)$ contributed to the solution by the $Li_3PO_4(s)$ that dissolves is negligibly small compared to 0.20 M. Then let y represent the molar concentration of $PO_4^{3-}(aq)$ present in the solution due to the $Li_3PO_4(s)$ that dissolves in the 0.20 M $LiNO_3$. Then $K_{sp} = 3.2 \times 10^{-9} = (0.20)^3(y) \Rightarrow y = \frac{3.2 \times 10^{-9}}{(0.20)^3} = 4.0 \times 10^{-7}\,M.$ So $[PO_4^{3-}(aq)] = [Li_3PO_4(aq)] = 4.0 \times 10^{-7}\,M$ in 0.20 M $LiNO_3(aq)$. Therefore, the number of moles of $Li_3PO_4(s)$ that can dissolve in 0.50 L of water is $0.50 \text{ L} \times \frac{4.0 \times 10^{-7} \text{ mol } Li_3PO_4}{1.0 \text{ L}} = \mathbf{2.0 \times 10^{-7} \text{ mol}}$	One point is earned for recognizing that $[Li^+]$ is approximately equal to 0.20 M in the solution to which the $Li_3PO_4(s)$ was added. One point is earned for a correct calculation of moles of Li_3PO_4.

Question 1 (continued)

The equation for the dissolution of $PbCl_2$ is shown below.

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ Cl^-(aq) \qquad K_{sp} = 1.6 \times 10^{-5} \text{ at } 25°C$$

(c) Calculate the concentration of $Cl^-(aq)$ in a saturated solution of $PbCl_2$ at 25°C.

Let $z = [Pb^{2+}]$ in a saturated solution of $PbCl_2$. Then $K_{sp} = [Pb^{2+}][Cl^-]^2 = (z)(2z)^2 = 4z^3$. Thus $1.6 \times 10^{-5} = 4z^3 \Rightarrow z = \sqrt[3]{\frac{1.6 \times 10^{-5}}{4}}$ $\Rightarrow z = [Pb^{2+}] = 1.6 \times 10^{-2}\ M$ $\Rightarrow [Cl^-] = 2[Pb^{2+}] = 2(1.6 \times 10^{-2}\ M) =$ **$3.2 \times 10^{-2}\ M$**	One point is earned for a correct setup. One point is earned for a correct calculation of the value of $[Cl^-]$.

(d) An open container holds 1.000 L of 0.00400 *M* $PbCl_2$, which is unsaturated at 25°C. Calculate the minimum volume of water, in mL, that must evaporate from the container before solid $PbCl_2$ can precipitate.

1.000 L of 0.00400 *M* $PbCl_2(aq)$ contains 0.00400 mol of $PbCl_2(aq)$, thus it contains 0.00400 mol $Pb^{2+}(aq)$ and 0.00800 mol $Cl^-(aq)$. Let V = volume of the solution at saturation, then $K_{sp} = 1.6 \times 10^{-5} = \left(\frac{0.00400 \text{ mol}}{V}\right)\left(\frac{0.00800}{V}\right)^2 = \frac{2.6 \times 10^{-7}}{V^3}$ $\Rightarrow V = \sqrt[3]{\frac{2.6 \times 10^{-7}}{1.6 \times 10^{-5}}} = 0.25 \text{ L} = 250 \text{ mL at saturation}$ Thus the volume of water that must evaporate = 1,000. − 250 = **750 mL** **OR** From part (c), the amount of $PbCl_2$ dissolved in 1 L of saturated $PbCl_2(aq)$ is $1.6 \times 10^{-2}\ M$. Let V = volume of the solution at saturation, then $\frac{0.016 \text{ mol } PbCl_2}{1{,}000 \text{ mL}} = \frac{0.00400 \text{ mol } PbCl_2}{V} \Rightarrow V = 250 \text{ mL}$ Thus the volume of water that must evaporate = 1,000. − 250 = **750 mL**	One point is earned for the calculation of the saturation volume. One point is earned for subtracting the saturation volume from 1,000 mL.

Question 2

Answer the following using chemical concepts and principles of the behavior of gases.

(a) A metal cylinder with a volume of 5.25 L contains 3.22 g of $He(g)$ and 11.56 g of $N_2(g)$ at 15.0°C.

(i) Calculate the total pressure in the cylinder.

$3.22\text{ g He} \times \frac{1.00\text{ mol He}}{4.00\text{ g He}} = 0.805\text{ mol He}$ $11.56\text{ g } N_2 \times \frac{1.00\text{ mol } N_2}{28.02\text{ g } N_2} = 0.4126\text{ mol } N_2$ total moles of gas $= (0.805 + 0.4126) = 1.218$ mol $P = \frac{nRT}{V} = \frac{(1.218\text{ mol})(0.0821\text{ L atm mol}^{-1}\text{K}^{-1})(15+273)\text{ K}}{5.25\text{ L}}$ $P =$ **5.49 atm**	One point is earned for the calculations of moles and adding them together. One point is earned for the correct substitution into the gas law equation. One point is earned for the correct answer.

(ii) Calculate the partial pressure of $N_2(g)$ in the cylinder.

pressure $N_2 = \frac{\text{moles } N_2 \text{ gas}}{\text{total moles of gas}} \times$ total pressure in flask $= \frac{0.4126\text{ mol}}{1.218\text{ mol}} \times 5.49\text{ atm} =$ **1.86 atm**	One point is earned for the calculation of the mole fraction of N_2. One point is earned for the correct answer.

(b) A 1.50 L container holds a 9.62 g sample of an unknown gaseous saturated hydrocarbon at 30°C and 3.62 atm.

(i) Calculate the density of the gas.

$D = \frac{m}{V} = \frac{9.62\text{ g}}{1.50\text{ L}} =$ **6.41 g L^{-1}**	One point is earned for the correct answer.

Question 2 (continued)

(ii) Calculate the molar mass of the gas.

Let $\boldsymbol{M}$ = molar mass, then $PV = nRT = \left(\frac{m}{\boldsymbol{M}}\right)RT \Rightarrow$ $\boldsymbol{M} = \frac{mRT}{PV} = \frac{(9.62\text{ g})(0.0821\text{ L atm K}^{-1}\text{mol}^{-1})(303\text{ K})}{(3.62\text{ atm})(1.50\text{ L})} = \mathbf{44.1\ g\ mol^{-1}}$	One point is earned for the correct answer.

(iii) Write the formula of the hydrocarbon.

Saturated hydrocarbons have the generic formula C_nH_{2n+2}, therefore let 44.1 g = 12(n) + 1(2n +2) = 14n + 2 $\Rightarrow$ 42.1 = 14n $\Rightarrow$ 3 = n $\Rightarrow$ $\mathbf{C_3H_8}$	One point is earned for the correct answer.

(iv) Calculate the root-mean-square speed of the gas molecules in the container at 30°C.
(Note: 1 J = 1 kg m^2 s^{-2})

$\upsilon_{\text{rms}} = \sqrt{\frac{3RT}{\boldsymbol{M}}} = \sqrt{\frac{3(8.31\text{ kg m}^2\text{s}^{-2}\text{ mol}^{-1}\text{ K}^{-1})(303\text{ K})}{0.0441\text{ kg mol}^{-1}}}$ $= \mathbf{414\ m\ s^{-1}}$	One point is earned for the correct setup using the molar mass in kilograms. One point is earned for the correct answer.

Question 3

A student performs a titration in which a 10.00 mL sample of 0.0571 *M* HCl is titrated with a solution of NaOH of unknown concentration.

(a) Describe the steps that the student should take to prepare and fill the buret for the titration given a wet 50.00 mL buret and the materials listed below.

0.0571 *M* HCl solution	Indicator solution
NaOH(*aq*) (unknown concentration)	Distilled water
10.5 *M* NaOH solution	100 mL beaker

Rinse the buret with some distilled water and then pour some of the NaOH solution of unknown concentration into the beaker and use it to rinse the buret two times. Use the beaker to carefully fill the buret with the NaOH solution of unknown concentration. Put the beaker under the buret and drain enough solution to remove any air bubbles in the neck and tip of the buret.	One point is earned for rinsing the buret with the titrant solution. One point is earned for removing air bubbles from the neck and tip of the buret.

(b) Calculate the pH of the 0.0571 *M* HCl.

HCl is a strong acid $\Rightarrow$ $[H^+]$ in 0.0571 *M* HCl = 0.0571 *M* pH = $-\log [H^+] = -\log (0.0571)$ = **1.243**	One point is earned for the correct answer.

(c) A volume of 7.62 mL of the NaOH solution was needed to reach the end point of the titration. Calculate the molarity of the NaOH solution used in the titration.

mol HCl titrated = $10.00 \text{ mL} \times \frac{0.0571 \text{ mol HCl}}{1{,}000 \text{ mL}} = 0.000571 \text{ mol}$; ratio HCl:NaOH in neutralization is 1:1, so 0.000571 mol NaOH reacted; $\frac{0.000571 \text{ mol NaOH}}{0.00762 \text{ L}}$ = **0.0749 *M* NaOH**	One point is earned for calculating the moles of HCl in the sample that was titrated. One point is earned for calculating the molarity of the NaOH solution.

Question 3 (continued)

In a different titration using a different NaOH solution, the concentration of NaOH was determined by the student to be 0.0614 *M*.

(d) Given that the actual concentration of the NaOH solution was 0.0627 *M*, calculate the percent error of the student's result.

$\text{percent error} = \frac{\lvert 0.0614 - 0.0627 \rvert}{0.0627} \times 100 = \mathbf{2.1\ \%}$	One point is earned for the correct answer.

(e) Calculate the volume of 10.5 *M* NaOH that is needed to prepare 250.0 mL of 0.0627 *M* NaOH.

$250.0\ \text{mL} \times \frac{0.0627\ \text{mol}}{1{,}000.\ \text{mL}} = 0.0157\ \text{mol NaOH needed}$	One point is earned for calculating the moles of NaOH needed.
$0.0157\ \text{mol NaOH} \times \frac{1{,}000.\ \text{mL}}{10.5\ \text{mol NaOH}} = \mathbf{1.49\ mL}$	One point is earned for the correct answer.

Question 4

For each of the following three reactions, in part (i) write a balanced equation and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be graded.

EXAMPLE:

A strip of magnesium metal is added to a solution of silver(I) nitrate.

(i) Balanced equation:

$$Mg + 2\,Ag^+ \longrightarrow Mg^{2+} + 2\,Ag$$

(ii) Which substance is oxidized in the reaction?

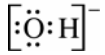
Mg is oxidized.

(a) Equal volumes of 0.1 *M* hydrofluoric acid and 0.1 *M* potassium hydroxide are combined.

(i) Balanced equation:

$$\mathbf{HF + OH^- \rightarrow F^- + H_2O}$$

(ii) Draw the complete Lewis electron-dot diagram for the reactant that is the Brønsted-Lowry base in the forward reaction.



(b) Solid calcium metal burns in air.

(i) Balanced equation:

$$\mathbf{2\,Ca + O_2 \rightarrow 2\,CaO}$$

(ii) Predict the algebraic sign of ΔH° for the reaction. Explain your prediction.

The sign of ΔH° will be negative because ΔG° is negative (the reaction occurs) and ΔS° is negative (a solid and a gas react to form a solid). According to the Gibbs-Helmholtz equation, $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$. Therefore ΔH° is the sum of two negative quantities and as such must be negative.

Question 4 (continued)

(c) Samples of nitrogen monoxide gas and oxygen gas are combined.

(i) Balanced equation:

$$\mathbf{2\ NO + O_2 \rightarrow 2\ NO_2}$$

(ii) If the reaction is second order with respect to nitrogen monoxide and first order with respect to oxygen, what is the rate law for the reaction?

$rate = k[NO]^2[O_2]$

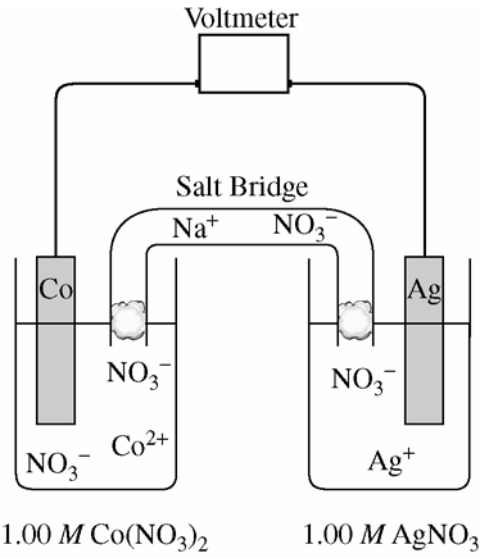
General Scoring Notes for Question 4

Five points are earned for each of parts (a), (b), and (c), distributed as follows.

Four points are earned for part (i): one point for the correct reactants, two points for the correct product(s), and one point for the correct coefficients in the balanced equation.

One point is earned for the correct answer in part (ii).

Question 5



Answer the following questions relating to the galvanic cell shown in the diagram above.

(a) Write the balanced equation for the overall cell reaction.

$2\ Ag^+(aq) + Co(s) \rightarrow 2\ Ag(s) + Co^{2+}(aq)$	One point is earned for the correct equation.

(b) Calculate the value of $E°$ for the cell.

$E°_{cell} = 0.80 - (-0.28) =$ **1.08 V**	One point is earned for the correct value of $E°_{cell}$.

(c) Is the value of $\Delta G°$ for the overall cell reaction positive, negative, or 0 ? Justify your answer.

The value of $\Delta G°$ for the overall reaction must be negative because the cell reaction occurs (is spontaneous) as the cell operates. OR Since $E°_{cell}$ is positive and $\Delta G° = -nFE°$, the value of $\Delta G°$ must be negative.	One point is earned for the correct answer, including a valid justification.

Question 5 (continued)

(d) Consider the cell as it is operating.

(i) Does E_{cell} increase, decrease, or remain the same? Explain.

As the cell operates, the concentration of Ag^+ decreases and the concentration of Co^{2+} increases $\Rightarrow$ the ratio $Q = \frac{[Co^{2+}]}{[Ag^+]^2}$ increases $\Rightarrow$ $\ln Q$ increases $\Rightarrow$ $E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$ becomes smaller (decreases).	One point is earned for the correct answer, including a valid justification.

(ii) Does ΔG of the overall cell reaction increase, decrease, or remain the same? Explain.

The value of ΔG for the system increases (becomes less negative) as the cell operates and the system approaches equilibrium (when $\Delta G = 0$).	One point is earned for the correct answer, including a valid justification.

(iii) What would happen if the $NaNO_3$ solution in the salt bridge was replaced with distilled water? Explain.

The cell would not operate. The voltage of the cell is too small to overcome the electrical resistance of distilled water, which is a poor conductor due to its very low concentration of ions (about 10^{-7} M $H^+(aq)$ and 10^{-7} M $OH^-(aq)$) that could "carry" the current from one cell to the other.	One point is earned for the correct answer, including a valid justification.

(e) After a certain amount of time, the mass of the Ag electrode changes by x grams. Given that the molar mass of Ag is 108 g mol^{-1} and the molar mass of Co is 59 g mol^{-1}, write the expression for the change in the mass of the Co electrode in terms of x.

$\Delta \text{ mol Ag} = \Delta \text{ mass Ag} \times \frac{1 \text{ mol Ag}}{108 \text{ g Ag}} = x \times \frac{1}{108} = \frac{x}{108}$ $\Delta \text{ mol Co} = -\Delta \text{ mol Ag} \times \frac{1 \text{ mol Co}}{2 \text{ mol Ag}} = -\frac{x}{108} \times \frac{1}{2} = -\frac{x}{216}$ $\Delta \text{ mass Co} = \Delta \text{ mol Co} \times \frac{59 \text{ g Co}}{1 \text{ mol Co}} = -\frac{x}{216} \times 59 = -\frac{59}{216}x$	One point is earned for using the correct mole ratio of Co to Ag. One point is earned for the correct answer (negative sign is not required).

Question 6

Answer each of the following using principles of atomic or molecular structure and/or intermolecular or intramolecular forces.

(a) Explain why the H–O–H bond angle in H_2O is less than the H–N–H bond angles in NH_3, as shown in the table below.

H–O–H Bond Angle in H_2O	H–N–H Bond Angles in NH_3
104.5°	107°

Both molecules have tetrahedral electron-domain geometries and might be expected to have bond angles of 109.5°. However, electron domains for nonbonding pairs of electrons exert a greater repulsion on adjacent pairs of electrons than do electron domains for bonding pairs. Thus, in the H_2O molecule with its <u>two</u> nonbonding pairs of electrons, the electron domains of bonding pairs are compressed to a greater extent than they are in the NH_3 molecule, which has only <u>one</u> nonbonding pair of electrons.	One point is earned for citing the difference in number of nonbonding pairs of electrons. One point is earned for citing the greater repulsion from nonbonding pairs as compared with bonding pairs.

(b) Explain why the radius of the Br atom is less than the radius of the Br^- ion, as shown in the table below.

Radius of Br	Radius of Br^-
0.111 nm	0.196 nm

The nuclear charge (+35) is the same for both the Br and Br^- species, but the "extra" electron in Br^- causes the electron cloud to expand due to an increase in mutual repulsions among the electrons that make up the cloud.	One point is earned for recognition that Br and Br^- have the same nuclear charge. One point is earned for citing increased repulsion among electrons.

Question 6 (continued)

(c) Explain why the dipole moment of HI is less than the dipole moment of HCl, as shown in the table below.

Dipole Moment of HI	Dipole Moment of HCl
0.42 debye	1.08 debyes

Iodine, having a lower electronegativity than chlorine has, forms a bond with hydrogen that is less polar than the bond between chlorine and hydrogen in HCl. The lower polarity of the $H–I$ bond means that the dipole moment of the bond is smaller than that of the $H–Cl$ bond.	One point is earned for citing the difference in electronegativity between I and Cl. One point is earned for the comparison of the polarity of the two bonds.

(d) Explain why the normal boiling point of Ne is less than the normal boiling point of Kr, as shown in the table below.

Normal Boiling Point of Ne	Normal Boiling Point of Kr
27 K	121 K

The intermolecular forces among atoms in liquid Ne are the same type of forces as those among atoms in liquid Kr, namely London (dispersion) forces. However, the magnitudes of these forces are smaller in Ne because the electron clouds of Ne atoms are smaller and less polarizable than the electron clouds of Kr atoms. Note: An explanation that cites only periodic trends or only the relative masses of Ne and Kr does not earn credit.	One point is earned for mentioning that intermolecular forces involved are London (dispersion) forces. One point is earned for mentioning the relative polarizability of the electron clouds of the atoms.