CHEMISTRY

Section I

Time—1 hour and 30 minutes

60 Questions

Note: For all questions, assume that the temperature is 298 K, the pressure is 1.0 atm, and solutions are aqueous unless otherwise specified.

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

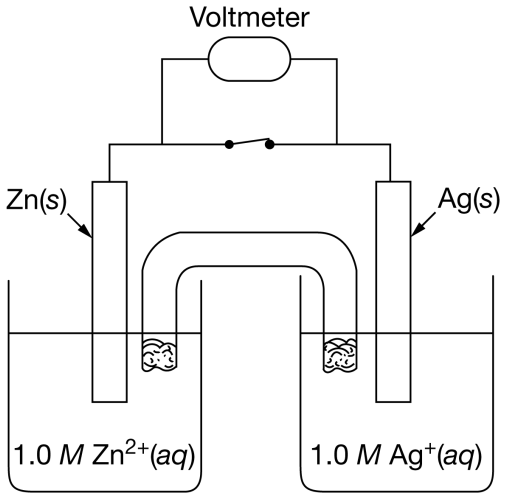
1. In his atomic theory, Dalton proposed that all atoms of a given element are identical. Which of the following observations provides the best evidence that the proposal is incorrect?

   (A) The mass spectrum of Cu has a peak at 63 amu and another peak at 65 amu.

   (B) The ionic radius of Cl^- is 0.181 nm, and the atomic radius of Cl is 0.079 nm.

   (C) The dipole moment of O_3 is 0.53 debye, and the dipole moment of O_2 is 0.00 debye.

   (D) Elemental P can exist in both white and red forms.



2. Which of the following substances would be the best choice for filling the salt bridge in the galvanic cell shown above, and why?

   (A) Distilled water, because it would avoid contaminating the solutions in the half-cells.

   (B) 1.0 *M* $HCl(aq)$, because it would acidify the solutions and catalyze the overall cell reaction.

   (C) 1.0 *M* $CH_3OH(aq)$, because it would increase the pH of the solutions and catalyze the overall cell reaction.

   (D) 1.0 *M* $KNO_3(aq)$, because the mobile ions would allow charge to flow between the half-cells.

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g) \qquad \Delta H^\circ < 0$$

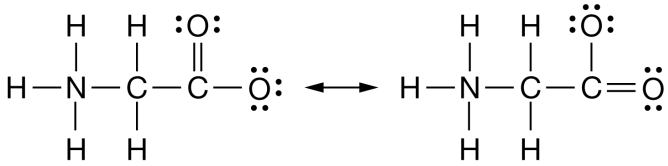
3. Which of the following statements must be true for the combustion of $CH_4(g)$, represented by the equation above?

   (A) The bond dissociation energy between O atoms in O_2 is greater than the sum of the bond dissociation energies of the two O−H bonds in H_2O.

   (B) More bonds are formed in the products than are broken in the reactants.

   (C) The sum of the bond dissociation energies of the product molecules is equal to the sum of the bond dissociation energies of the reactant molecules.

   (D) The sum of the bond dissociation energies of the product molecules is greater than the sum of the bond dissociation energies of the reactant molecules.



4. Based on the resonance structures shown above, what are the bond orders of the two carbon-oxygen bonds?

   (A) 1 and 1.5

   (B) 1 and 2

   (C) 1.5 and 1.5

   (D) 2 and 2

Mass of Solid	Mass of Water	ΔT_{water}
1.0 g	2000 g	+2.1 °C

5. A sample of a solid organic compound is completely combusted in a calorimeter. The heat generated by combustion is transferred to the water, causing the temperature of the water to increase. Based on the data in the table above, which of the following is the best estimate of the heat of combustion, ΔH_{comb}, of the organic solid? (The specific heat of water is 4.2 J/(kg·°C).)

   (A) +18 kJ/g

   (B) +8.4 kJ/g

   (C) −8.4 kJ/g

   (D) −18 kJ/g

Substance	Specific Heat (J/(kg·°C))	Mass of sample (g)
Fe(s)	0.46	1.0
Al(s)	0.91	1.0

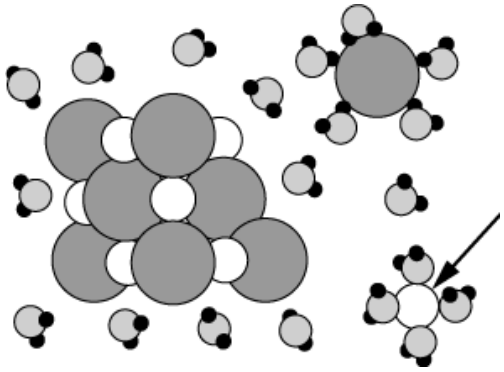
6. Samples of Fe and Al are heated from 25°C to 55°C. Based on the information in the table above, the change in the average kinetic energy of the atoms in the samples is

   (A) higher for the sample Fe, because with its lower specific heat it absorbs more energy

   (B) higher for the sample Al, because with its lower specific heat it absorbs more energy

   (C) the same for both metal samples, because the initial and final temperatures are the same

   (D) the same for both metal samples, because the masses are equal



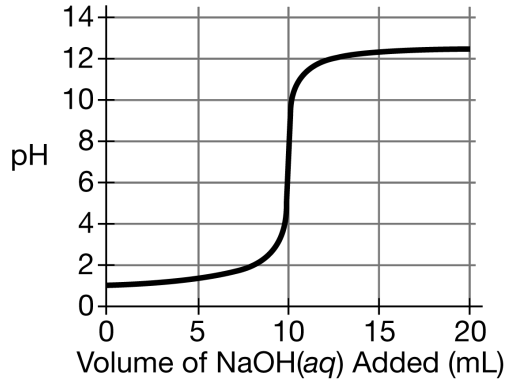
7. An ionic crystal is added to water and starts to dissolve as shown in the particulate representation above. Based on the orientation of the water molecules, what can be assumed about the charge of the hydrated particle indicated by the arrow?

   (A) The particle is positively charged, because the oxygen atoms in water are attracted to it.

   (B) The particle is negatively charged, because hydrogen atoms in water are attracted to it.

   (C) The particle is both positively and negatively charged, because the water molecules are attracted to it.

   (D) The particle is neutral, because the dipoles of the water molecules neutralize the charge of the particle.



8. A 20.0 mL sample of a 0.125 M monoprotic acid solution is titrated with a solution of NaOH(aq) unknown concentration. Based on the titration curve above, what is the molar concentration of the NaOH(aq) solution?

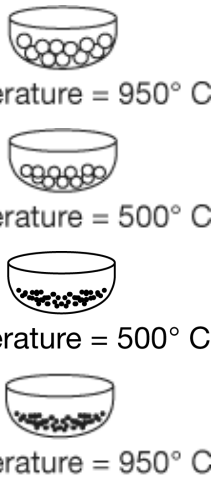
   (A) 0.063 M
   (B) 0.125 M
   (C) 0.250 M
   (D) 0.500 M

$$\text{HOCN}(aq) \rightleftharpoons \text{H}^+(aq) + \text{OCN}^-(aq) \qquad K_a = 3 \times 10^{-4}$$

9. The ionization of cyanic acid, HOCN, is represented above. A certain solution of HOCN has a pH of 2.0. What is the approximate concentration of unionized in the HOCN(aq) solution?

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

10. Two solid reactants of varying particle size are combined in a vessel. Assuming that the same mass of each reactant is used in each case, which of the following represents the conditions that will result in the fastest reaction rate?



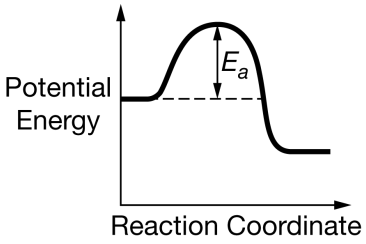
Questions 11-13

$$4\text{FeS}(s) + 7\text{O}_2(s) \rightarrow 2\text{Fe}_2\text{O}_3(s) + 4\text{SO}_2(g)$$

Due to the presence of $\text{Fe}(s)$ as an impurity, the combustion of some types of coal results in the formation of $\text{SO}_2(g)$, as represented by the equation above. Also, $\text{SO}_2(g)$ can react with $\text{O}_3(g)$ to form $\text{SO}_3(g)$, as represented by the equation below.

$$\text{SO}_2(g) + \text{O}_3(g) \rightleftharpoons \text{SO}_3(g) + \text{O}_2(g)$$
$$\Delta H^\circ_{298} = -242 \text{ kJ/mol}_{\text{rxn}} \qquad \Delta S^\circ_{298} = -25 \text{ J/(K·mol}_{\text{rxn}})$$

11. Which of the following diagrams shows the correctly labeled activation energy, E_a, for the reaction between $\text{SO}_2(g)$ and $\text{O}_3(g)$?

(A)


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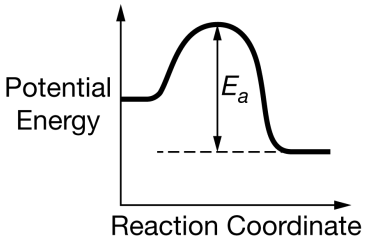

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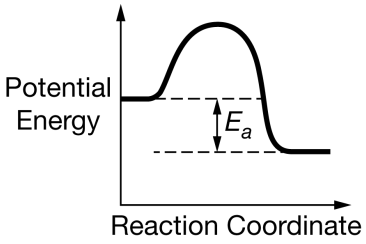
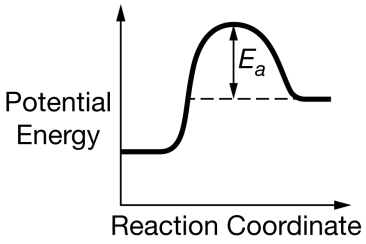


(D)


12. Which of the following statements is correct when 2.0 mol of $\text{FeS}(s)$ reacts with 4.0 mol of $\text{O}_2(g)$?

(A) $\text{O}_2(g)$ is the limiting reactant and 2.0 mol of $\text{SO}_2(g)$ is formed.

(B) $\text{O}_2(g)$ is the limiting reactant and 4.0 mol of $\text{SO}_2(g)$ is formed.

(C) $\text{FeS}(g)$ is the limiting reactant and 4.0 mol of $\text{SO}_2(g)$ is formed.

(D) $\text{FeS}(g)$ is the limiting reactant and 0.5 mol of $\text{O}_2(g)$ remains unreacted.

13. Which of the following is most likely to be true about the reaction between $\text{SO}_2(g)$ and $\text{O}_3(g)$ at 298 K?

(A) $\Delta G^\circ < 0$ and $T\Delta S^\circ$ is smaller in magnitude than ΔH°.

(B) $\Delta G^\circ < 0$ and $T\Delta S^\circ$ is larger in magnitude than ΔH°.

(C) $\Delta G^\circ > 0$ and $T\Delta S^\circ$ is smaller in magnitude than ΔH°.

(D) $\Delta G^\circ > 0$ and $T\Delta S^\circ$ is larger in magnitude than ΔH°.

Solution	pK_a
$HF(aq)$	3.17
$HC_2H_3O_2(aq)$	4.74
$NH_4^+(aq)$	9.26

14. Based on the information in the table above, which of the following pairs of solutions can be used to create a buffer with a pH of 9.3? (Assume all solutions are 1.0 M.)

    (A) 100.0 mL of $HC_2H_3O_2(aq)$ and 50.0 mL of $KOH(aq)$

    (B) 50.0 mL of $HF(aq)$ and 50.0 mL of $NaF(aq)$

    (C) 100.0 mL of $NH_3(aq)$ and 100.0 mL of $HCl(aq)$

    (D) 50.0 mL of $NH_3(aq)$and 50.0 mL of $NH_4Cl(aq)$

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \; \Delta G^\circ = -234 \text{ kJ/mol}_{\text{rxn}}$$

15. The value of ΔG° for the reaction represented above implies that the decomposition of $H_2O_2(aq)$ is thermodynamically favorable. However, $H_2O_2(aq)$ is typically stable for up to a year stored in a dark bottle at 298 K. The best explanation for this observation is that the decomposition reaction

    (A) is only thermodynamically favorable in the presence of a catalyst

    (B) occurs with an increase in entropy because $O_2(g)$ is a product

    (C) is reversible and $H_2O_2(aq)$ is produced almost as fast as it decomposes

    (D) has a slow rate at 298 K because the activation energy is relatively high

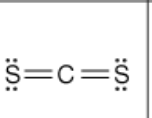
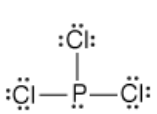
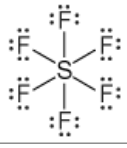
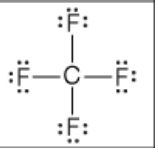
16. The equilibrium constant 1.0 for a reaction is greater than at temperatures above 500 K but less than 1.0 at temperatures below 500 K. What can be concluded about the values of ΔH° and ΔS° for the reaction? (Assume that ΔH° and ΔS° are independent of temperature.)

    (A) $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$

    (B) $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$

    (C) $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$

    (D) $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$

CS_2	PCl_3	SF_6	CF_4
			

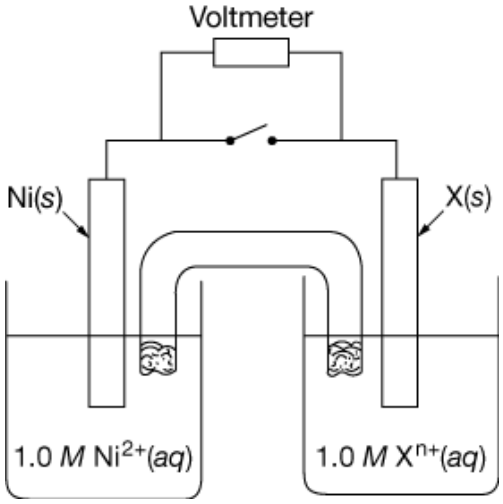
17. Based on the diagrams shown above, which of the following would have the greatest dipole moment, and why?

    (A) CS_2, because the double bonds create an area of higher electron density around the C atom.

    (B) PCl_3, because the Cl atoms draw electron density away from the P atom and the bond dipoles do not cancel one another.

    (C) SF_6, because it has the greatest number of polar bonds.

    (D) CF_4, because the large electronegativity difference between C and F results in very polar bonds.



18. In the galvanic cell shown above, the voltmeter connected across the electrodes shows a voltage of 0.52 V. Based on the standard reduction potentials given in the table below, which of the following is most likely the identity of the unknown element, X?

Half-reaction	E°(V)
$Rh^{3+}(aq) + 3e^- \rightarrow Rh(s)$	0.76
$Bi^{3+}(aq) + 3e^- \rightarrow Bi(s)$	0.31
$In^{+}(aq) + e^- \rightarrow In(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.24
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76

(A) Rh

(B) Bi

(C) In

(D) Zn

19. A 30 g sample of Al(s) is heated to 50°C and placed in a calorimeter containing of 150 g water at 20°C. As the system approaches thermal equilibrium, energy is transferred

(A) from the Al(s) to the water and the temperature of the water decreases

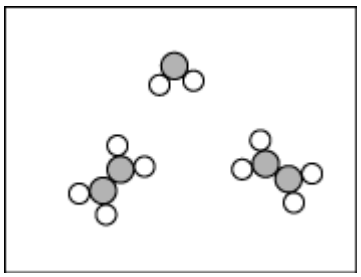
(B) from the Al(s) to the water and the temperature of the Al(s) decreases

(C) from the water to the Al(s) and the temperature of the water increases

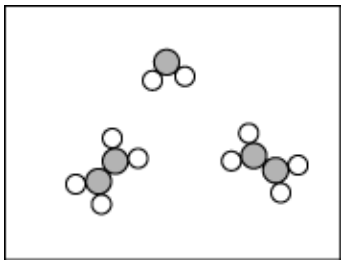
(D) from the water to the Al(s) and the temperature of the Al(s) increases

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = 200$$

20. The equilibrium system shown above is represented in the diagram below in which each molecule represents one mole of the substance in a 100L container at a constant temperature.



Additional $N_2O_4(g)$ is added to the container and allowed to reestablish equilibrium. Which of the following best represents the system after the equilibrium has been reestablished?

(A)


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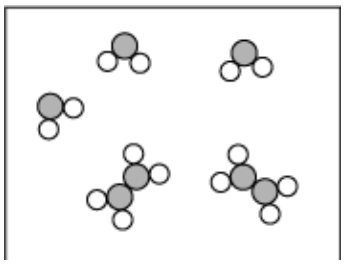

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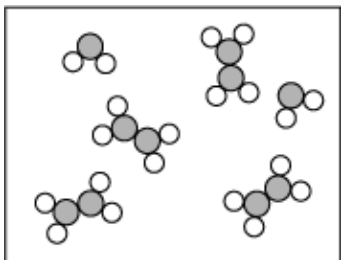

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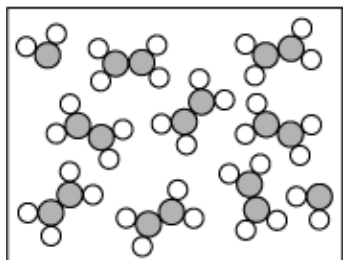


Compound	Melting Point (°C)
MgO	2852
NaF	993

21. The table above shows the melting points of $MgO(s)$ and $NaF(s)$. Which of the following best helps explain why the melting point of $MgO(s)$ is much higher than that of $NaF(s)$?

(A) The mass of F^- ions is greater than that of O^{2-} ions.

(B) The mass of Mg^{2+} ions is greater than that of Na^+ ions.

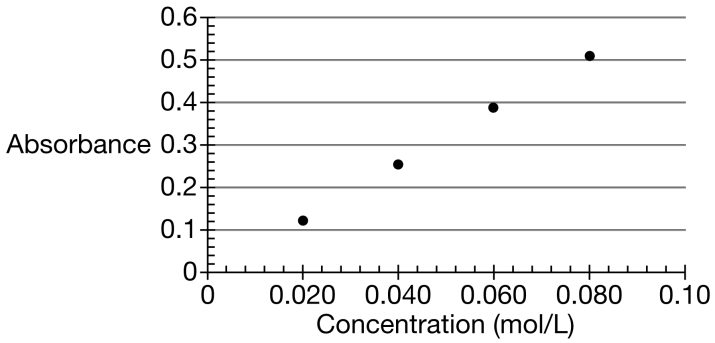
(C) The difference between the electronegativity values of Mg and O is smaller than the difference between the values of Na and F.

(D) The charges of Mg^{2+} and O^{2-} ions are greater than those of Na^+ and F^- ions.

Questions 22-25

An experiment was performed to investigate the reaction between Zn metal and $Ni^{2+}(aq)$ at different concentrations. Because the ion is green, the extent of the reaction was determined using spectrophotometric analysis. Four 20.0 mL standard solutions of $Ni^{2+}(aq)$ were prepared by dissolving $NiCl_2{\cdot}6H_2O$ (molar mass 240 g/mol) in water. The absorbance of each solution was measured; the results are shown both in the table below and in the following plot of the absorbance data.

Solution	$[Ni]^{2+}$	Absorbance
1	0.020	0.12
2	0.040	0.25
3	0.060	0.39
4	0.080	0.51



22. The concentration of $Cl^-(aq)$ ions in solution 2 was

    (A) 0.020 *M*
    (B) 0.040 *M*
    (C) 0.060 *M*
    (D) 0.080 *M*

23. Which of the following equations best represents the reacting species in the reaction between Zn metal and $NiCl_2(aq)$

    (A) $Zn(s) + NiCl_2(aq) \rightarrow Zn^{2+}(aq) + Ni(s) + 2Cl^-(aq)$
    (B) $Zn(s) + NiCl_2(aq) \rightarrow ZnCl_2(aq) + Ni^{2+}(aq)$
    (C) $Zn^{2+}(aq) + Ni(s) \rightarrow Zn(s) + Ni^{2+}(aq)$
    (D) $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$

24. What is the expected absorbance of a standard solution made by dissolving 0.0070 mol of $NiCl_2{\cdot}6H_2O$ in water to make 100 mL of solution?

    (A) 0.0039
    (B) 0.0080
    (C) 0.045
    (D) 0.45

25. Which species is being oxidized in the reaction between Zn metal and $NiCl_2(aq)$?

    (A) Zn
    (B) Zn^{2+}
    (C) Ni
    (D) Ni^{2+}

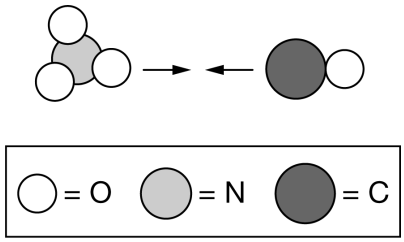
26. A sample of a pure compound is analyzed and found to contain approximately 30 percent N and 70 percent O by mass. The formula for the compound could be

(A) NO

(B) NO_2

(C) N_2O

(D) N_2O_2



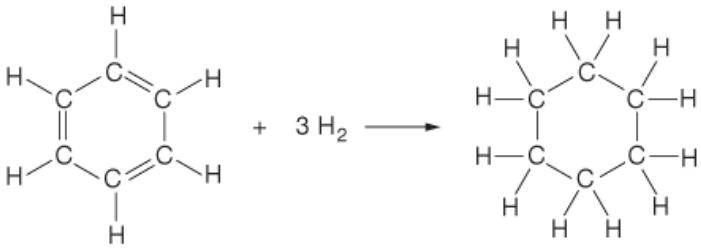
27. The slowest step in a reaction mechanism requires the collision represented above to occur. Which of the following most likely indicates how the addition of a solid catalyst could increase the rate of the reaction?

(A) The catalyst could change the reaction from second order to third order.

(B) The catalyst could increase the particles' speed, thereby increasing the value of the rate constant, k.

(C) The catalyst could decrease the particles' speed, making it less likely that the particles will rebound without reacting when they collide.

(D) The catalyst could adsorb one of the particles, making a successful (reaction-producing) collision with the other particle more likely.



28. In the reaction represented above, which of the following sets correctly identifies the hybridization of the C atoms before and after the reaction occurs?

Set	Before	After
A	sp^2	sp^2
B	sp^2	sp^3
C	sp^3	sp^2
D	sp^3	sp^3

(A) Set A

(B) Set B

(C) Set C

(D) Set D

29. A student finds the mass of a pure sample of a metal chloride hydrate. The student heats the sample several times, reaching a constant mass that contains 0.100 mole of anhydrous metal chloride. Which of the following questions about the hydrated metal chloride substance is most likely to be answered by the results of the experiment?

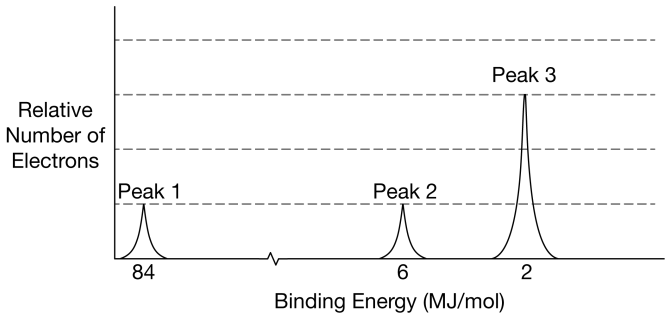
(A) How many moles of water are in one mole of the substance?

(B) How many moles of the metal cation are in one mole of the substance?

(C) What is the identity of the metal cation in the formula of the substance?

(D) What is the melting point of the substance?

Questions 30-31



The complete photoelectron spectrum of a pure element is shown in the diagram above.

30. According to the complete photoelectron spectrum, which of the following is the identity of the element?

(A) Be
(B) C
(C) O
(D) Ne

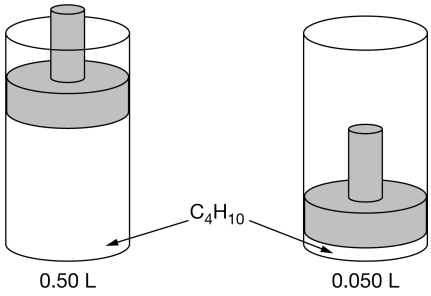
31. If peaks 1 and 2 represent *s* sublevels, which of the following sublevels is represented by peak 3?

(A) *s*
(B) *p*
(C) *d*
(D) *f*

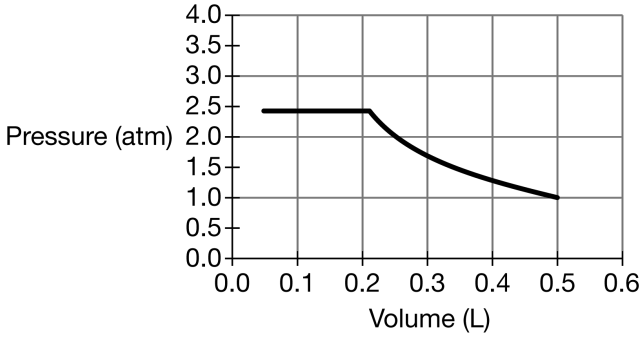
32. In an experiment to estimate the enthalpy change of a reaction, a student makes two aqueous solutions, each containing one of the reactants. The student combines the solutions, both originally at the same temperature, in a calorimeter and records the final temperature of the mixture. In addition to the masses of the solutions and the temperature change of the mixture, which of the following pieces of information does the student need to calculate the enthalpy change of the reaction?

(A) The density of the reaction mixture
(B) The specific heat capacity of the reaction mixture
(C) The boiling point of the reaction mixture
(D) The heat of fusion of the reaction mixture

Questions 33-35



A sample of $C_4H_{10}(g)$ is placed in a rigid vessel with a movable piston. The volume of the gas is reduced by moving the piston downward while the temperature is maintained at 25°C, as shown above. The pressure of the gas versus its volume is plotted in the graph below.



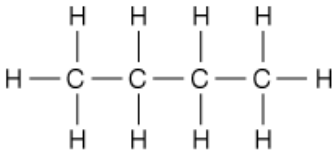
33. Which of the following best explains the increase in pressure of the $C_4H_{10}(g)$ when its volume is decreased from 0.50 L to 0.21 L?

    (A) The molecules strike the walls of the vessel more frequently.

    (B) The molecules strike the walls of the vessel with different orientations.

    (C) The molecules strike the walls of the vessel with greater force.

    (D) The molecules decompose to produce a greater number of particles.



34. The Lewis electron-dot diagram for C_4H_{10} is shown above. Which of the following is the predominant type of intermolecular force among C_4H_{10} molecules?

    (A) Hydrogen bonding

    (B) London dispersion forces

    (C) Dipole-dipole attractions

    (D) Dipole-induced dipole attractions

35. Which of the following best accounts for the pressure in the vessel remaining constant as the volume decreases below 0.21 L?

    (A) The density of the $C_4H_{10}(g)$ increases.

    (B) The surface area of the interior of the vessel decreases.

    (C) The temperature of the $C_4H_{10}(g)$ decreases.

    (D) Some $C_4H_{10}(g)$ condenses to form $C_4H_{10}(l)$.

36. Which of the following substances has bonds with the greatest ionic character?

(A) CCl_4

(B) $CuCl_2$

(C) $CaCl_2$

(D) NCl_3

$HOCl(aq)$	$K_a = 3.0 \times 10^{-8}$
$HC_2H_3O_2(aq)$	$K_a = 1.8 \times 10^{-5}$
$NH_3(aq)$	$K_b = 1.8 \times 10^{-5}$
$C_6H_5NH_2(aq)$	$K_b = 3.0 \times 10^{-10}$

37. The K_a or K_b values of some weak acids and bases are listed in the table above. Which of the following solutions has the highest pH?

(A) 0.1 *M* $HOCl(aq)$

(B) 0.1 *M* $HC_2H_3O_2(aq)$

(C) 0.1 *M* $NH_3(aq)$

(D) 0.1 *M* $C_6H_5NH_2(aq)$

$$ICl(g) \rightleftharpoons \frac{1}{2} I_2(g) + \frac{1}{2} Cl_2(g) \quad K_{eq} = 0.1$$

38. Based on the information above, what is the value of for the reaction represented k_{eq} below?

$$I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g)$$

(A) 0.01

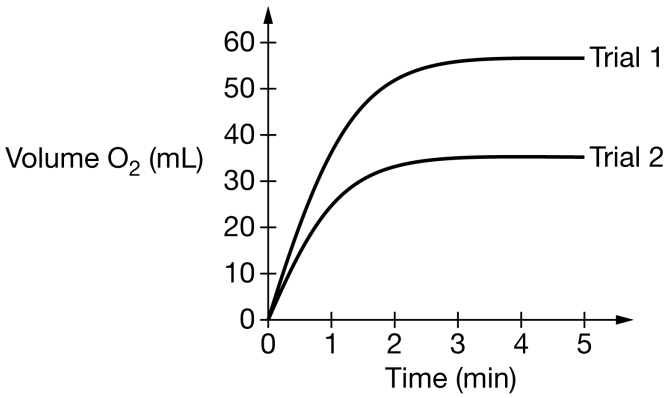
(B) 10

(C) 20

(D) 100

$$2\ H_2O_2 \xrightarrow{KI(s)} 2\ H_2O(l) + O_2(g)$$
$$\text{Rate} = k[H_2O_2]$$

39. A student performed an experiment to study the factors that affect the rate of the first-order catalytic decomposition of $H_2O_2(aq)$, represented above.



The student monitored the volume of $O_2(g)$ produced over time as the reaction proceeded. The data from two trials are plotted in the graph above. Which of the following best explains the results of trial 2 compared with those of trial 1?

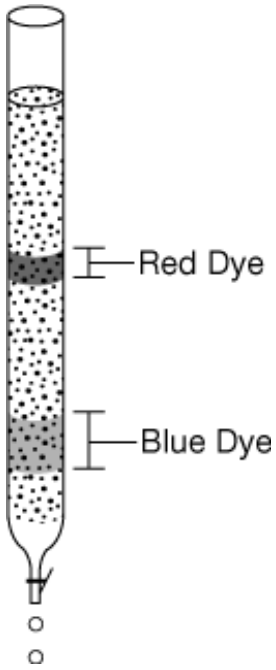
(A) The reaction temperature in trial 2 was higher than it was in trial 1.

(B) The volume of the reaction vessel was larger in trial 2 than it was in trial 1.

(C) The student used a smaller amount of $KI(s)$ in trial 2 compared with that used in trial 1.

(D) The concentration of $H_2O_2(aq)$ was lower in trial 2 than it was in trial 1.

Questions 40-42



A student placed a sample of a food coloring that contains a mixture of a blue dye and a red dye at the top of a chromatography column filled with a nonpolar stationary phase. When water is poured through the column, two bands of colors are seen in the column, as shown in the diagram above.

40. Which of the following techniques would be best to investigate molecular vibrations in molecules of the red dye?

    (A) Infrared spectroscopy

    (B) UV/vis spectroscopy

    (C) Mass spectrometry

    (D) Gravimetric analysis

41. A student collects a sample of the blue dye from the column in a cuvette. Which of the following is <u>least</u> useful to determine the concentration of the sample using a spectrophotometer set at 640 nm?

    (A) The volume of the sample

    (B) The path length of the cuvette

    (C) The absorbance of the dye at 640 nm

    (D) The molar absorptivity of the dye at 640 nm

42. Which of the following will most likely be observed if $CH_3OH(l)$ is used in the column instead of water? (Assume that both solvents flow through the column at the same rate.)

    (A) The dyes will not pass through the column because $CH_3OH(l)$ is a nonpolar solvent.

    (B) The dyes will pass through the column at a slower rate because $CH_3OH(l)$ is a less polar solvent than water.

    (C) The dyes will pass through the column at a faster rate because $CH_3OH(l)$ has a greater molar mass than water.

    (D) No differences will be observed because the polarity of the solvent does not affect the separation of the dyes.

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq) \quad K_{sp} = 8.1 \times 10^{-9}$$

43. The dissolution of $BaCO_3(s)$ in water is represented above. A 20.0 mL sample of 1.0×10^{-4} M $Ba(NO_3)_2(aq)$ is mixed with an 80.0 mL sample of 1.0×10^{-4} M $Na_2CO_3(aq)$. Which of the following correctly predicts and explains the outcome?

(A) A precipitate will form, because $Q = 1.0 \times 10^{-8}$.

(B) A precipitate will form, because $Q = 1.6 \times 10^{-9}$.

(C) A precipitate will not form, because $Q = 1.0 \times 10^{-8}$.

(D) A precipitate will not form, because $Q = 1.6 \times 10^{-9}$.

Compound	$[Pb^{2+}]$ in Saturated Solution
PbS	1.7×10^{-14} M
$PbCO_3$	2.7×10^{-7} M
$PbCrO_4$	5.5×10^{-7} M
$PbSO_4$	1.6×10^{-4} M

44. Based on $[Pb^{2+}]$ in saturated solutions of the compounds listed in the table above, which of the compounds has the smallest K_{sp} value?

(A) PbS

(B) $PbCO_3$

(C) $PbCrO_4$

(D) $PbSO_4$

Cl^-	Ar	K^+	Ca^{2+}

45. The four species above have the same electron configuration, $1s^2 2s^2 s2p^6 3s^2 3p^6$. Which of the following statements correctly identifies the species with the largest radius and provides an explanation based on Coulomb's law?

(A) Cl^-, because its nuclear charge exerts the least attractive force on the electrons in the $3p$ sublevel.

(B) Ar, because it is a neutral atom and the net force on the electrons in the $3p$ sublevel is zero.

(C) K^+, because the loss of an electron results in a smaller attractive force between the nucleus and the electrons in the $3p$ sublevel.

(D) Ca^{2+}, because the large positive charge on a cation causes increased repulsion among the electrons in the $3p$ sublevel.

$$2\ H_2(g) + 2\ NO(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

46. The experimental rate law for the reaction represented above is rate$= k[H_2][NO]^2$. Which of the following proposed mechanisms is consistent with the rate law?

	Step 1:	$2\ NO \rightarrow N_2O_2$	fast
(A)	Step 2:	$H_2 + N_2O_2 \rightleftharpoons N_2O + H_2O$	fast
	Step 3:	$H_2 + N_2O \rightarrow N_2 + H_2O$	slow
	Step 1:	$2\ NO \rightleftharpoons N_2O_2$	fast
(B)	Step 2:	$H_2 + N_2O_2 \rightarrow N_2O + H_2O$	slow
	Step 3:	$H_2 + N_2O \rightarrow N_2 + H_2O$	fast
	Step 1:	$2\ NO \rightarrow N_2 + O_2$	slow
(C)	Step 2:	$H_2 + O_2 \rightarrow H_2O_2$	fast
	Step 3:	$H_2 + H_2O_2 \rightarrow 2\ H_2O$	fast
	Step 1:	$2\ NO \rightarrow N_2 + O_2$	fast
(D)	Step 2:	$H_2 + O_2 \rightleftharpoons H_2O_2$	fast
	Step 3:	$H_2 + H_2O_2 \rightarrow 2\ H_2O$	slow

47. Which of the following equations represents a reaction with a negative ΔS°?

(A) $2\ NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(B) $2\ KClO_3(g) + 2\ KCl(s) \rightarrow 3O_2(g)$

(C) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

(D) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

$$CO(g) + 3\ H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$
$$K_p = 66 \text{ at } 500\ ^\circ\text{C}$$

48. At a certain time, the partial pressure of the gases in the reaction mixture represented above had the values shown in the table below.

P_{CO}	P_{H_2}	P_{CH_4}	P_{H_2O}
0.02 atm	1.0 atm	0.4 atm	0.4 atm

Based on the information above, which of the following occurred as the reaction mixture moved toward equilibrium?

(A) More $CH_4(g)$ was produced because the rate of the forward reaction was higher than the rate of the reverse reaction.

(B) More $H_2(g)$ was produced because the rate of the reverse reaction was higher than the rate of the forward reaction.

(C) More $CH_4(g)$ was produced because the total pressure of the $H_2(g)$ and $CO(g)$ combined was higher than that of the products; thus the reaction shifted to the side with the fewest number of moles of gas.

(D) More $H_2(g)$ was produced because the pressure of $CO(g)$ was the least and the reaction shifted to the side with the smaller number of moles of gas.

49. $CCl_4(g)$ deviates more from ideal gas behavior than $CH_4(g)$ does. Which of the following statements best explains this observation?

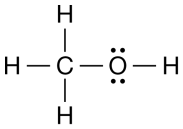
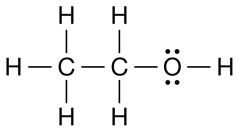
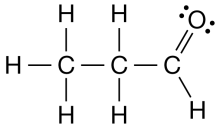
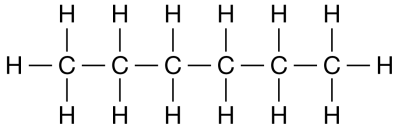
(A) The mass of the CCl_4 molecule is greater than that of the CH_4 molecule.

(B) The bond energy of the C−Cl bond is greater than that of the C−H bond.

(C) The dipole-dipole forces between CCl_4 molecules are greater than those between CH_4 molecules.

(D) The London dispersion forces between CCl_4 molecules are stronger than those between CH_4 molecules.

Questions 50-52 refer to the table below.

Compound	Structure	Boiling Point (°C)
Methanol		65
Ethanol		78
Propanal		49
Hexane		69

50. A 50 mL sample of $C_6H_{14}(l)$ is mixed with a 50 mL sample of $H_2O(l)$, and the mixture is shaken vigorously. The two liquids do not stay mixed but instead form two separate layers. The density of hexane is 0.66 g/mL, and the density of water is 1.00 g/mL. A 1.0 g sample of $I_2(s)$ is added to the mixture, which is shaken again. Which of the following best predicts what happens to the $I_2(s)$?

    (A) I_2 will be found mainly in the top layer because it will dissolve more in the $H_2O(l)$.

    (B) I_2 will be found mainly in the bottom layer because it will dissolve more in the $H_2O(l)$.

    (C) I_2 will be found mainly in the top layer because it will dissolve more in the $C_6H_{14}(l)$.

    (D) I_2 will be found mainly in the bottom layer because it will dissolve more in the $C_6H_{14}(l)$.

51. When a 50 mL sample of C_2H_5OH is mixed with a 50 mL sample of H_2O, the resulting mixture has a volume of 95 mL, and the container is warm to the touch. Which of the following best describes these observations?

    (A) A chemical reaction occurs, as evidenced by the volume of the resultant mixture being less than the total volume of the initial components.

    (B) A chemical change occurs, as evidenced by the formation of new covalent bonds releasing more energy than is absorbed by the breaking of the existing covalent bonds.

    (C) A physical change occurs, and the solvation process is exothermic.

    (D) A physical change occurs, and the solvation process is endothermic

52. Which of the following best helps to explain why hexane has a higher boiling point than methanol has?

    (A) Methanol molecules can form hydrogen bonds with other methanol molecules.

    (B) Hexane cannot form hydrogen bonds with other hexane molecules.

    (C) Methanol molecules have attractions to one another due to London dispersion forces.

    (D) Hexane molecules have electron clouds that are larger than those of methanol molecules.

53. A 0.08 M solution of CH_3COOH(p$K_a = 4.74$)is titrated with 0.10 M NaOH(aq). What is the pH at the equivalence point of the titration and why?

(A) pH < 7, because NaOH(aq) is a strong base.

(B) pH = 7, because the titration reaction is a neutralization reaction.

(C) pH > 7, because $CH_3COO^-(aq)$ is a weak base.

(D) pH > 7, because the concentration of NaOH(aq) is greater than that of $CH_3COOH(aq)$.

$[Co(H_2O)_6]^{2+} + 4\ Cl^- \rightarrow [CoCl_4]^{2-} + 6\ H_2O(l)$
pink blue

54. The solvent in the nonaqueous system represented above is 2-propanol. If a small amount of water is added to the system, how will the color of the solution be affected, and why?

(A) The solution will become more pink because more $[Co(H_2O)_6]^{2+}$ will be produced.

(B) The solution will become more pink because the pH of the solution will increase.

(C) The solution will become more blue because more $[CoCl_4]^{2-}$ will be produced.

(D) The solution will become more blue because the pH of the solution will decrease.

Element	Second Ionization Energy (kJ/mol)
Li	7300
Na	4560
K	3050
Rb	2630

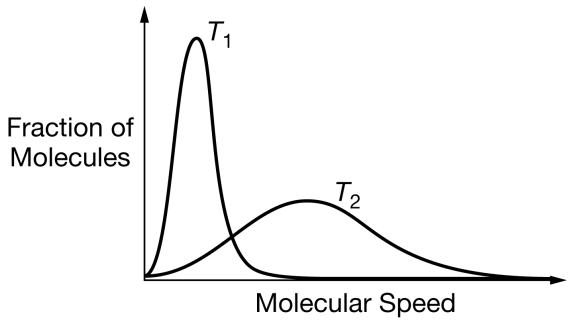
55. The decrease in the second ionization energy of alkali metals going down the group, as shown in the table above, can be best attributed to a decrease in the coulombic force of attraction due to

(A) the removal of core electrons

(B) an increase in effective nuclear charge

(C) an increase in the average distance of the outermost electron from the nucleus

(D) a decrease in electron-electron repulsion within the outermost shell



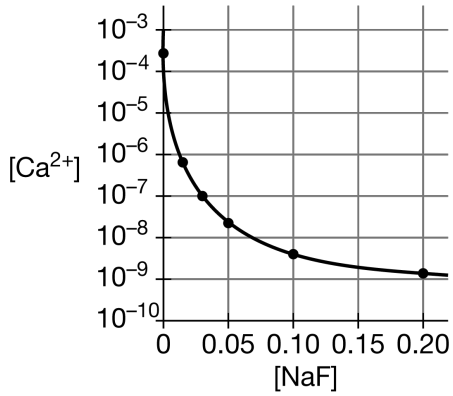
56. The diagram above shows the distribution of molecular speed in a sample of gas at two different temperatures, T_1 and T_2. Which of the following is a correct interpretation of the information provided by the diagram?

(A) The average speed of the molecules is greater at T_1 than at T_2.

(B) The taller peak corresponds to the higher temperature, T_1.

(C) There are fewer molecules of gas at T_2 than at T_1.

(D) The average kinetic energy of the molecules is greater at than T_2 at T_1.



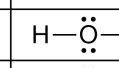
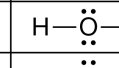
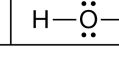
57. Which of the following statements best explains the trend in the molar solubility of $CaF_2(s)$ in various concentrations of NaF(aq) shown in the graph above?

(A) Higher concentrations of $F^-(aq)$ allow less $CaF_2(s)$ to dissolve before the solution becomes saturated.

(B) Higher concentrations of $Na^+(aq)$ lead to more favorable attractions between $Na^+(aq)$ ions and $F^-(aq)$ ions, thus less $CaF_2(s)$ dissolves.

(C) Higher concentrations of $F^-(aq)$ produce more $OH^-(aq)$ through hydrolysis, causing $Ca(OH)_2(s)$ to precipitate, thus more $CaF_2(s)$ dissolves.

(D) Higher concentrations of $F^-(aq)$ cause the formation of the $CaF_4^{2-}(aq)$ complex ion, which allows more $CaF_2(s)$ to dissolve.

Acid	Structure
HClO	
HBrO	
HIO	

58. A 0.1 *M* aqueous solution of which of the acids shown in the table above would have a pH closest to 7.0, and why?

(A) HClO, because Cl has the highest electronegativity.

(B) HBrO, because Br has the lowest electronegativity.

(C) HIO, because I has the lowest electronegativity.

(D) All three solutions will have the same pH because they are all monoprotic acids.

59. The value of K_w at 37°C is 2.4×10^{-14}. Which of the following statements about the pH and pOH of pure water at 37°C is correct?

(A) pH < 7 and pOH > 7 because water dissociates to a lesser extent at 37°C than at 25°C.

(B) pH > 7 and pOH < 7 because the dissociation of water is endothermic, and pH + pOH = 14.

(C) pH = pOH < 7 because because water dissociates to a greater extent at 37°C than at 25°C.

(D) pH = pOH = 7 because $[H_3O^+] = [OH^-]$ for pure water.

$$NH_3(aq) + CH_3NH_3^+(aq) \rightleftharpoons NH_4^+(aq) + CH_3NH_2(aq) \; K_{eq} = 0.041$$

60. Which of the following species is the strongest base in the reaction represented above?

(A) $NH_3(aq)$

(B) $CH_3NH_3^+(aq)$

(C) $CH_4^+(aq)$

(D) $CH_3NH_2(aq)$

STOP
END OF SECTION I

CHEMISTRY

Section II

Time—1 hour and 45 minutes

7 Questions

Note: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Directions: Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

1. Answer the following questions related to NH_3.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ_{298} = -92.2\text{kJ/mol}_{\text{rxn}};\ \Delta S^\circ_{298} = -198.8\ \text{J/(mol}_{\text{rxn}}\cdot\text{K)}$$

(a) The reaction of $N_2(g)$ and $H_2(g)$ to form $NH_3(g)$ is represented above. The reaction has been studied in order to maximize the yield of $NH_3(g)$.

i. Calculate the value of ΔG°, in kJ/mol$_{\text{rxn}}$, at 298K.

ii. Calculate the value of the equilibrium constant, K_p, at 298K.

Bond	Average Bond Enthalpy (kJ/moL)
N−H	391
H−H	436
N≡N	?

(b) Based on the average bond enthalpies in the table above and the value of ΔH°_{298}, calculate the value of the N≡N bond enthalpy.

(c) Although the reaction is thermodynamically favorable at 298 K, it does not occur to an observable extent at this temperature. Explain how the N≡N bond enthalpy affects the rate of the reaction.

(d) The reaction is usually carried out at a very high temperature in the presence of a catalyst. Explain why the reaction is thermodynamically unfavorable at very high temperatures. Justify your answer in terms of ΔH°, ΔS°, and their effect on ΔG°.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(e) Although the forward reaction represented above is thermodynamically unfavorable at very high temperatures, it can be used to produce NH_3 if the NH_3 is continually removed from the reaction vessel. Explain in terms of Q and K_p why this method works.

The boiling points of H_2 and NH_3 are given in the table below.

Substance	Boiling Point
H_2	20 K
NH_3	240 K

(f) A student claims that $H_2(g)$ condenses at a much lower temperature than $NH_3(g)$ because H_2 has stronger intermolecular forces than NH_3 does. There are two errors in the student's reasoning. Identify the student's errors and explain your answer in terms of the specific types of forces involved.

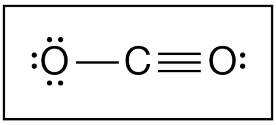


Diagram *X*

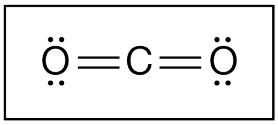


Diagram *Z*

2. Answer the following questions related to CO_2.

   (a) Two possible Lewis electron-dot diagrams for CO_2 are shown above. Explain in terms of formal charges why diagram *Z* is the better diagram.

   (b) Identify the hybridization of the valence orbitals of the C atom in the CO_2 molecule represented in diagram *Z*.

   (c) A 0.1931 mol sample of dry ice, $CO_2(s)$, is added to an empty balloon. After the balloon is sealed, the $CO_2(s)$ sublimes and the $CO_2(g)$ in the balloon eventually reaches a temperature of 21.0 °C and pressure of 0.998 atm. The physical change is represented by the following equation.

$$CO_2(s) \rightarrow CO_2(g) \qquad \Delta H_{\text{sublimation}} = ?$$

      i. What is the sign (positive or negative) of the enthalpy change for the process of sublimation? Justify your answer.

      ii. List all the numerical values of the quantities, with appropriate units, that are needed to calculate the volume of the balloon.

      iii. Calculate the final volume, in liters, of the balloon.

   (d) $CO_2(g)$ reacts with water to form $H_2CO_3(aq)$, which quickly ionizes in water to form $HCO_3^-(aq)$ and $H_3O^+(aq)$, as shown in the following equation.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

      i. Identify one of the conjugate acid-base pairs in the equation above.

      ii. When the concentration of CO_2 in water increases, more H_2CO_3 forms. Does the increase in the formation of H_2CO_3 cause the value of the reaction quotient, *Q*, for the system to increase, decrease, or remain the same? Justify your answer.

   (e) A student investigates the acid-base properties of $HCO_3^-(aq)$. The reaction of $HCO_3^-(aq)$ with $H_2O(l)$ is represented below.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

      i. The student measured the pH of a 0.100 *M* solution of $HCO_3^-(aq)$ as 9.68. Calculate the concentration of $OH^-(aq)$ in the solution.

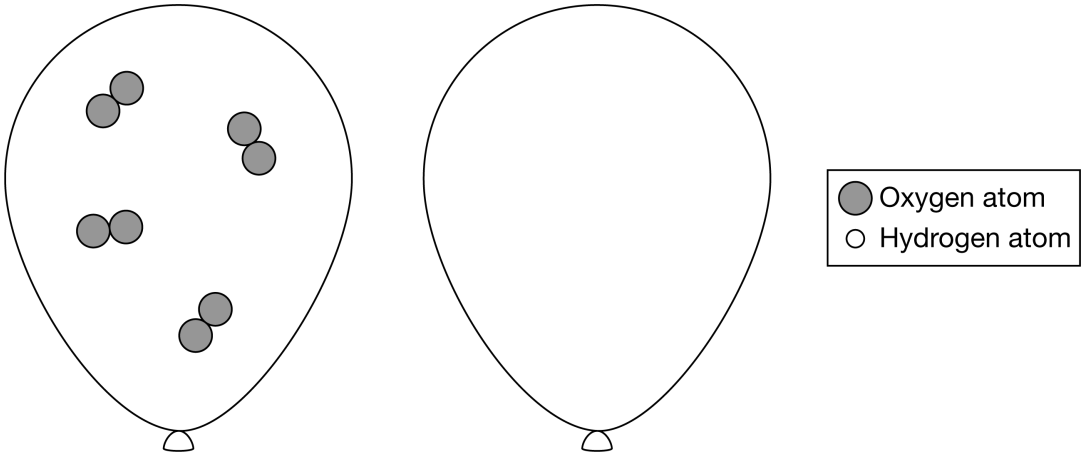
$$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$$

      ii. The K_b expression for the reaction of $HCO_3^-(aq)$ with $H_2O(l)$ is given above. Calculate the value of K_b for the reaction.

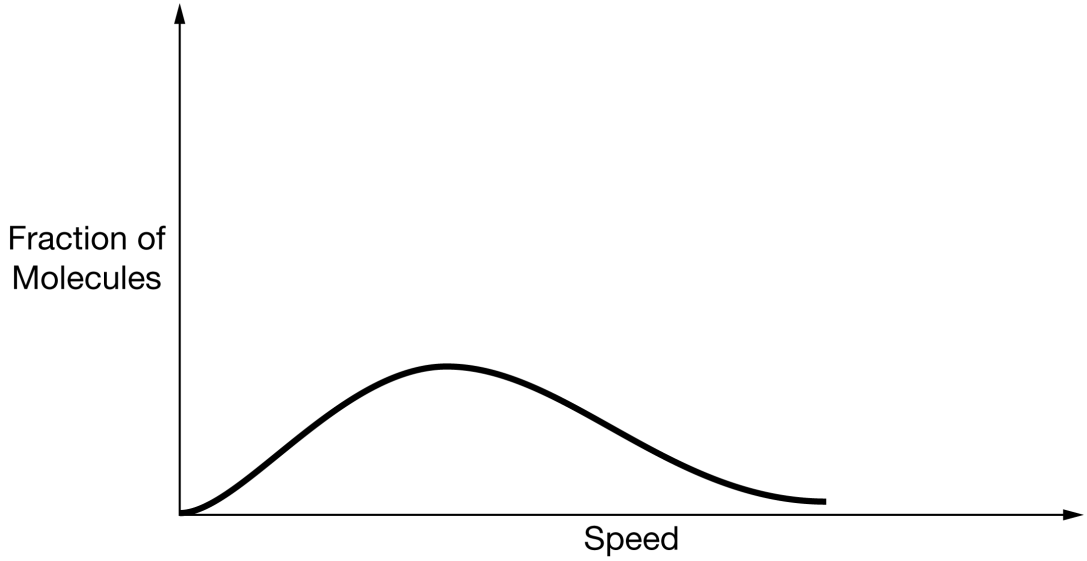
      iii. The student then carried out a second experiment at the same temperature to determine K_b. In the experiment, the student measured the pH of 0.300 *M* $HCO_3^-(aq)$. Would the value of K_b calculated in the second experiment be greater than, less than, or equal to the value of K_b calculated in part (e)(ii)? Justify your answer.

3. Answer the following questions about hydrogen and oxygen gases.

(a) A particle-level representation of $O_2(g)$ is shown in the balloon below on the left. The balloon on the right contains the same volume of $H_2(g)$ at the same temperature and pressure. In the balloon on the right, draw a representation of $H_2(g)$ with the appropriate number and distribution of particles.

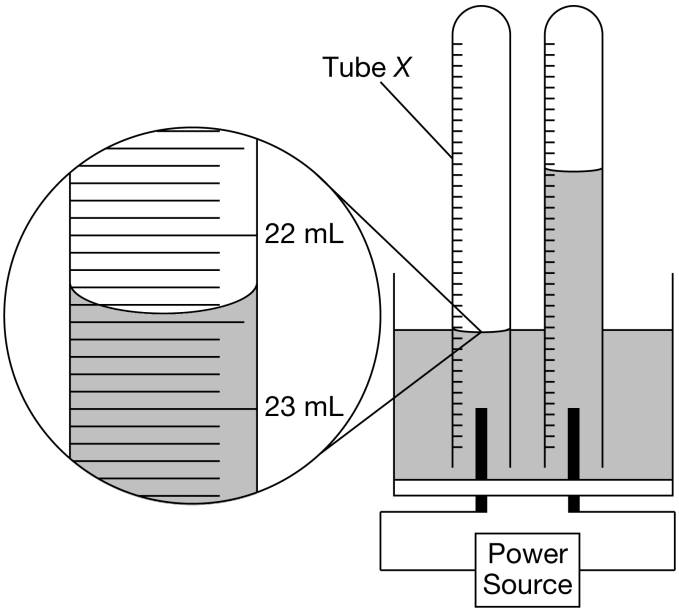


(b) The graph below shows the Maxwell-Boltzmann distribution for $H_2(g)$. On the same graph, draw the distribution curve for $O_2(g)$ at the same temperature.



$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

To generate the $H_2(g)$ and the $O_2(g)$, a student performs electrolysis of water, represented by the equation above. The student collects the gases in tubes and then adjusts the position of one of them so that the water levels inside and outside of the tube are the same, as shown in the following diagram.



(c) Is the gas collected in tube X $H_2(g)$ or $O_2(g)$? Justify your answer.

(d) What volume should the student report for the gas in tube X?

(e) Is $H_2(g)$ produced at the anode or cathode? Justify your answer in terms of oxidation numbers.

(f) The atmospheric pressure in the lab was 0.989 atm at 22.0°C. The vapor pressure of water at 22.0°C is 0.026 atm. Calculate the pressure of dry gas in tube X.

(g) The value of E° for the electrolysis of water is -1.23V. In a second trial of the experiment, the power source was replaced with a voltmeter. Would the volume of hydrogen gas produced be greater than, less than, or equal to the volume produced in the original experiment? Justify your answer.

(h) The student considers the reverse reaction and proposes a mechanism with a single, elementary step as shown below.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Explain, in terms of particle collisions, why this mechanism is unlikely to be correct.

4. A student wishes to determine the concentration of $Ag^+(aq)$ in a solution of $AgNO_3(aq)$. The student combines 10.00 mL of $AgNO_3(aq)$ with excess $Na_2SO_4(aq)$ and observes the formation of a white precipitate. The formation of the precipitate is represented by the following equation.

$$2AgNO_3(aq) + Na_2SO_4(aq) \rightarrow Ag_2SO_4(s) + 2NaNO_3(aq)$$

(a) Write the balanced net ionic equation for the precipitation reaction.

The student collects the precipitate by filtration and measures the mass of the filter paper and precipitate every 10 minutes as it dries. The student records the data in the following table.

Mass of dry filter paper	0.88 g
Mass of filter paper and precipitate immediately after filtration	4.82 g
Mass of filter paper and precipitate after 10 minutes	4.37 g
Mass of filter paper and precipitate after 20 minutes	4.01 g
Mass of filter paper and precipitate after 30 minutes	3.79 g

(b) Use the data above to calculate the number of moles of $Ag_2SO_4(s)$ (molar mass 311.8 g/mol) that precipitated.

(c) Calculate the concentration of $Ag^+(aq)$ in the original 10.00 mL solution of $AgNO_3(aq)$.

(d) The concentration of $Ag^+(aq)$ determined by the student is significantly higher than the actual concentration of $Ag^+(aq)$. Based on the student's data table, identify an error in the experimental procedure that led to this result.

5. A student determines the mass percent of iron in a sample of iron ore by doing a redox titration. The student finds the mass of the sample and then dissolves it in acid to a total volume of 25.00 mL. Using a buret, the student titrates the 25.00 mL solution with 0.017 M $K_2Cr_2O_7$. The following reaction occurs during the titration.

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^{+}(aq) ß 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

The student collects the following data.

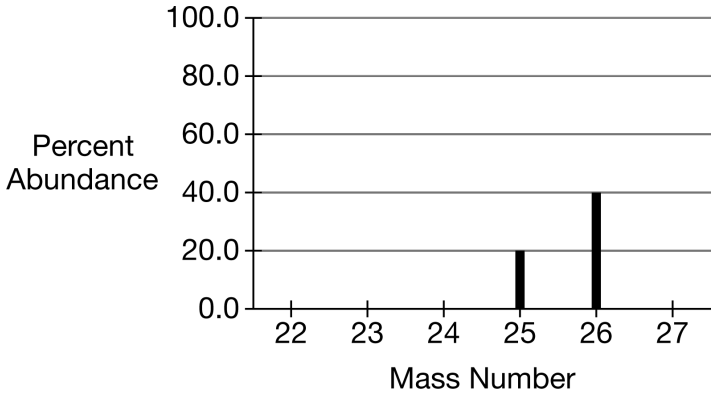
Mass of iron ore in original sample	0.36 g
Buret reading at end point	45.52mL
Initial buret reading	15.05mL

(a) How many moles of $Fe^{2+}(aq)$ reacted with the $Cr_2O_7^{2-}(aq)$?

(b) Assuming that all the iron in the ore was Fe^{2+}, calculate the mass percent of iron in the ore sample.

(c) The student learns that the actual mass percent of iron in the ore sample is greater than the experimental value calculated in part (b). The student claims that the difference between the actual and experimental values could have been caused by rinsing the buret with distilled water just prior to filling it with 0.017 M $K_2Cr_2O_7(aq)$. Do you agree with the student's claim? Explain your reasoning.

6. The three stable isotopes of Mg are Mg-24, Mg-25, and Mg-26. A rock sample from another planet has a different distribution of the three stable isotopes than what is found on Earth. A partial mass spectrum for Mg in the rock sample is shown below.



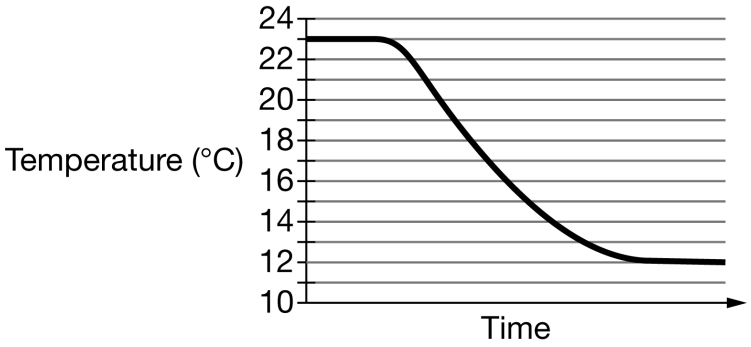
(a) Draw a line on the graph to show the mass of the missing isotope and its percent abundance.

(b) Use the completed mass spectrum to calculate the average atomic mass of Mg on the other planet.

(c) The first ionization energy of magnesium samples found on Earth is experimentally determined to be 736 kJ/mol. If a similar experiment is conducted to determine the first ionization energy of magnesium in the rock sample from another planet, will it be greater than, less than, or equal to the first ionization energy of magnesium found on Earth? Explain your reasoning.

	Successive Ionization Energies (kJ/mol)		
	First	Second	Third
Mg	736	1450	7740
Unknown element	496	4560	6910

(d) A table of successive ionization energies for Mg and an unknown element is shown above. Predict the identity of the unknown element.



7. A student conducts an experiment to determine the value of $\Delta H^\circ_{\text{soln}}$ for the dissolution of $NaC_2H_3O_2(s)$. The student dissolves 10.0 g of $NaC_2H_3O_2(s)$ in room-temperature water in a beaker and measures the temperature over time. The data are given in the graph above.

   (a) The student touches the side of the beaker after the dissolution has occurred and observes that it is cold. What experimental evidence is consistent with the student's observation?

   (b) Is the dissolution of $NaC_2H_3O_2(s)$ endothermic or exothermic? Justify your answer in terms of the flow of energy between the system and surroundings.

   (c) The student calculated the energy change for the dissolution to be 4600 J. Based on this value, calculate $\Delta H^\circ_{\text{soln}}$ in kJ/mol.