CHEMISTRY

Section I

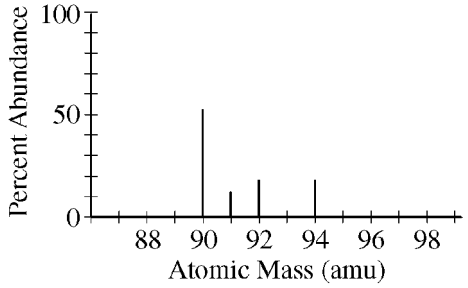
50 Questions

Time—90 minutes

CALCULATORS ARE NOT ALLOWED FOR SECTION I.

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. The mass spectrum of an average sample of a pure element is shown in the figure above. Which of the following is the identity of the element?

   (A) Y
   (B) Zr
   (C) Nb
   (D) Th

2. The ideal gas law best describes the properties of which of the following gases at 0°C and 1 atm?

   (A) PH_3
   (B) HBr
   (C) SO_2
   (D) N_2

3. At 298 K and 1 atm, Br_2 is a liquid with a high vapor pressure, and Cl_2 is a gas. Those observations provide evidence that under the given conditions, the

   (A) forces among Biz molecules are stronger than those among Cl_2 molecules
   (B) forces among Cl molecules are stronger than the Cl−Cl bond
   (C) Br-Br bond is stronger than the Cl-Cl bond
   (D) Cl−Cl bond is stronger than the Br−Br bond

4. Which of the following has the bonds arranged in order of decreasing polarity?

   (A) H–F > N–F > F–F
   (B) H–I > H–Br > H–F
   (C) O–N > O–S > O–Te
   (D) Sb–I > Sb–Te > Sb–Cl

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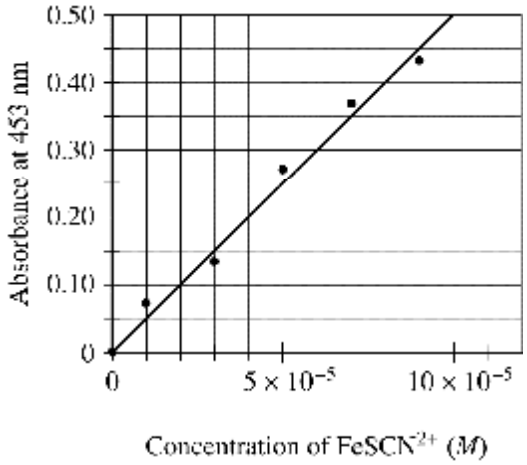
$$Fe^{3+}(aq) + KSCN(s) \rightarrow FeSCN^{2+}(aq) + K^{+}(aq)$$

5. To determine the moles of $Fe^{3+}(aq)$ in a 100. mL sample of an unknown solution, excess $KSCN(s)$ is added to convert all the $Fe^{3+}(aq)$ into the dark red species $FeSCN^{2+}(aq)$, as represented by the equation above. The absorbance of $FeSCN^{2+}(aq)$ at different concentrations is shown in the graph below.



If the absorbance of the mixture is 0.20 at 453 nm, how many moles of $Fe^{3+}(aq)$ were present in the 100. mL sample? (Assume that any volume change due to adding the $KSCN(s)$ is negligible.)

(A) 4×10^{-4} mol
(B) 3×10^{-4} mol
(C) 4×10^{-6} mol
(D) 3×10^{-6} mol

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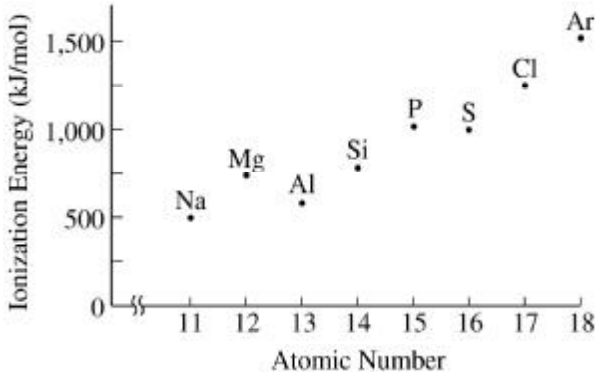
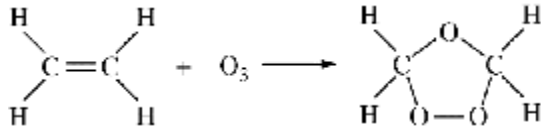


6. The first ionization energy of an element is the energy required to remove an electron from a gaseous atom of the element (i.e., $X(g) \rightarrow X^+(g) + e^-$). The values of the first ionization energies for the third-row elements are shown in the graph above. On the basis of the information given, which of the following reactions is exothermic?

(A) $Cl(g) + Mg^+(g) \rightarrow Cl^+(g) + Mg(g)$
(B) $Al(g) + Mg^+(g) \rightarrow Al^+(g) + Mg(g)$
(C) $P(g) + Mg^+(g) \rightarrow P^+(g) + Mg(g)$
(D) $S(g) + Mg^+(g) \rightarrow S^+(g) + Mg(g)$



7. In the reaction represented above, what is the hybridization of the C atoms before and after the reaction occurs?

	Before	After
(A)	sp	sp^2
(B)	sp	sp^3
(C)	sp^2	sp
(D)	sp^2	sp^3

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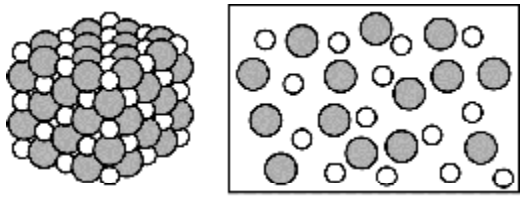

Solid MgO Liquid MgO

8. Based on the diagram above, which of the following best helps to explain why MgO(*s*) is not able to conduct electricity, but MgO(*l*) is a good conductor of electricity?

(A) MgO(*s*) does not contain free electrons, but MgO(*l*) contains free electrons that can flow.

(B) MgO(*s*) contains no water, but MgO(*l*) contains water that can conduct electricity.

(C) MgO(*s*) consists of separate Mg^{2+} ions and O^{2-} ions, but MgO(*l*) contains MgO molecules that can conduct electricity.

(D) MgO(*s*) consists of separate Mg^{2+} ions and O^{2-} ions held in a fixed lattice, but in MgO(*l*) the ions are free to move and conduct electricity.

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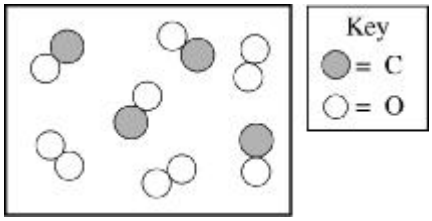
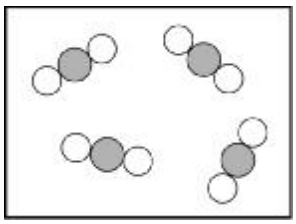
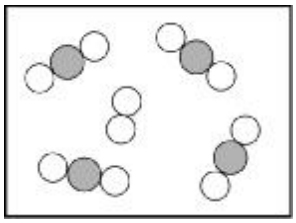
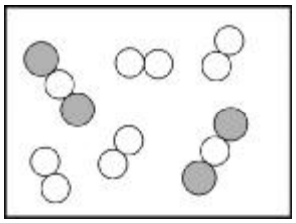
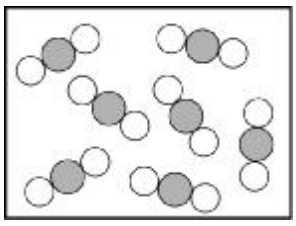


9. A mixture of $CO(g)$ and $O_2(g)$ is placed in a container, as shown above. A reaction occurs, forming $CO_2(g)$. Which of the following best represents the contents of the box after the reaction has proceeded as completely as possible?

(A) 

(B) 

(C) 

(D) 

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Questions 10-13 refer to the following information.

$$Cu(s) + 4\ HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\ NO_2(g) + 2\ H_2O(l)$$

Each student in a class placed a 2.00 g sample of a mixture of Cu and Al in a beaker and placed the beaker in a fume hood. The students slowly poured 15.0 mL of 15.8 *M* $HNO_3(aq)$ into their beakers. The reaction between the copper in the mixture and the $HNO_3(aq)$ is represented by the equation above. The students observed that a brown gas was released from the beakers and that the solutions turned blue, indicating the formation of $Cu^{2+}(aq)$. The solutions were then diluted with distilled water to known volumes.

10. Which of the following is true about the reaction?

(A) It is a Brønsted-Lowry acid-base reaction, because the solution is neutral at the end.

(B) It is a Brønsted-Lowry acid-base reaction, because $HNO_3(aq)$ is a strong acid.

(C) It is a redox reaction, because $Cu(s)$ is oxidized and $H^+(aq)$ is reduced.

(D) It is a redox reaction, because $Cu(s)$ is oxidized and the nitrogen atom in $NO_3^-(aq)$ is reduced.

$[Cu^{2+}]$	Absorbance
0.025	0.059
0.050	0.235
0.100	0.117
0.200	0.468
Unknown (from sample of mixture)	0.330

11. To determine the number of moles of Cu in the sample of the mixture, the students measured the absorbance of known concentrations of $Cu(NO_3)_2(aq)$ using a spectrophotometer. A cuvette filled with some of the solution produced from the sample of the mixture was also tested. The data recorded by one student are shown in the table above. On the basis of the data provided, which of the following is a possible error that the student made?

(A) The $Cu(NO_3)_2(aq)$ from the sample of the mixture was not diluted properly.

(B) The spectrophotometer was calibrated with tap water instead of distilled water.

(C) The student labeled the cuvettes incorrectly, reversing the labels on two of the solutions of known concentration.

(D) The spectrophotometer was originally set to an inappropriate wavelength, causing the absorbance to vary unpredictably.

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12. The students determined that the reaction produced 0.010 mol of $Cu(NO_3)_2$. Based on the measurement, what was the percent of Cu by mass in the original 2.00 g sample of the mixture?

(A) 16%
(B) 32%
(C) 64%
(D) 96%

13. In one student's experiment the reaction proceeded at a much slower rate than it did in the other students' experiments. Which of the following could explain the slower reaction rate?

(A) In the student's sample the metal pieces were much smaller than those in the other students' samples.

(B) The student heated the reaction mixture as the $HNO_3(aq)$ was added.

(C) The student used a 1.5 *M* solution of $HNO_3(aq)$ instead of a 15.8 *M* solution of $HNO_3(aq)$.

(D) The student used a 3.00 g sample of the mixture instead of the 2.00 g sample that was used by the other students.

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14. A student is given a sample of a pure, white crystalline substance. Which of the following would be most useful in providing data to determine if the substance is an ionic compound?

(A) Examining the crystals of the substance under a microscope
(B) Determining the density of the substance
(C) Testing the electrical conductivity of the crystals
(D) Testing the electrical conductivity of an aqueous solution of the substance

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Ne, HF, C_2H_6, CH_4

15. Which of the substances listed above has the highest boiling point, and why?

(A) Ne, because its atoms have the largest radius
(B) HF, because its molecules form hydrogen bonds
(C) CHo, because each molecule can form multiple hydrogen bonds
(D) CH_4, because its molecules have the greatest London dispersion forces

16. A sample of a solid labeled as NaCl may be impure. A student analyzes the sample and determines that it contains 75 percent chlorine by mass. Pure NaCl(*s*) contains 61 percent chlorine by mass. Which of the following statements is consistent with the data?

(A) The sample contains only NaCl(*s*).
(B) The sample contains NaCl(*s*) and NaI(*s*).
(C) The sample contains NaCl(*s*) and KCl(*s*).
(D) The sample contains NaCl(*s*) and LiCl(*s*).

17. If a pure sample of an oxide of sulfur contains 40. percent sulfur and 60. percent oxygen by mass, then the empirical formula of the oxide is

(A) SO_3
(B) SO_4
(C) S_2O_6
(D) S_2O_8

18. When 4.0 L of He(*g*), 6.0 L of N_2(*g*), and 10. L of Ar(*g*), all at 0°C and 1.0 atm, are pumped into an evacuated 8.0 L rigid container, the final pressure in the container at 0°C is

(A) 0.5 atm
(B) 1.0 atm
(C) 2.5 atm
(D) 4.0 atm

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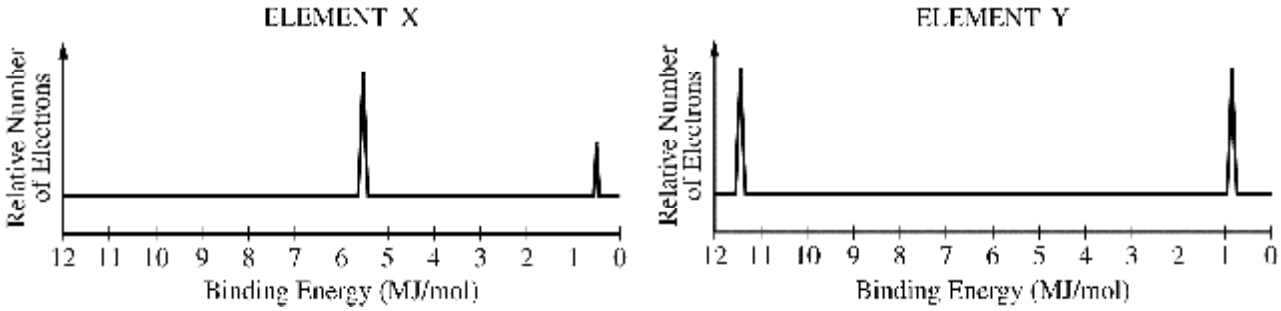

19. The complete photoelectron spectra of neutral atoms of two unknown elements, X and Y, are shown above. Which of the following can be inferred from the data?

(A) Element X has a greater electronegativity than element Y does.
(B) Element X has a greater ionization energy than element Y does.
(C) Element Y has a greater nuclear charge than element X does.
(D) The isotopes of element Y are approximately equal in abundance, but those of element X are not.

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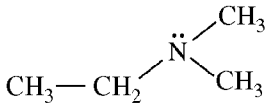
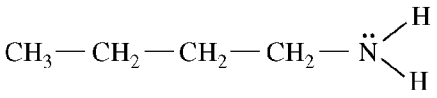


Compound 1



Compound 2

20. Based on the structures shown above, which of the following statements identifies the compound with the higher boiling point and provides the best explanation for the higher boiling point?

(A) Compound 1, because it has stronger dipole-dipole forces than compound 2
(B) Compound 1, because it forms hydrogen bonds, whereas compound 2 does not
(C) Compound 2, because it is less polarizable and has weaker London dispersion forces than compound 1
(D) Compound 2, because it forms hydrogen bonds, whereas compound 1 does not

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21. On the basis of molecular structure and bond polarity, which of the following compounds is most likely to have the greatest solubility in water?

(A) CH_4
(B) CCl_4
(C) NH_3
(D) PH_3

Questions 22-25 refer to the following information.

$$\underset{\text{colorless}}{N_2O_4(g)} \rightleftarrows \underset{\text{brown}}{2\,NO_2(g)} \qquad K_p = 3.0 \text{ at } 70^\circ C$$

A mixture of $NO_2(g)$ and $N_2O_4(g)$ is placed in a glass tube and allowed to reach equilibrium at 70°C, as represented above.

22. If $P_{N_2O_4}$ is 1.33 atm when the system is at equilibrium at 70°C, what is P_{NO_2} ?

(A) 0.44 atm
(B) 2.0 atm
(C) 2.3 atm
(D) 4.0 atm

23. Which of the following statements best helps to explain why the contents of the tube containing the equilibrium mixture turned a lighter color when the tube was placed into an ice bath?

(A) The forward reaction is exothermic.
(B) The forward reaction is endothermic.
(C) The ice bath lowered the activation energy.
(D) The ice bath raised the activation energy.

24. Which of the following best predicts how the partial pressures of the reacting species will be affected if a small amount of Ar(*g*) is added to the equilibrium mixture at constant volume?

(A) P_{NO_2} will decrease and $P_{N_2O_4}$ will increase.
(B) P_{NO_2} will increase and $P_{N_2O_4}$ will decrease.
(C) Both P_{NO_2} and $P_{N_2O_4}$ will decrease.
(D) No change will take place.

25. Which of the following statements about ΔH° for the reaction is correct?

(A) $\Delta H^\circ < 0$ because energy is released when the N–N bond breaks.
(B) $\Delta H^\circ < 0$ because energy is required to break the N–N bond.
(C) $\Delta H^\circ > 0$ because energy is released when the N–N bond breaks.
(D) $\Delta H^\circ > 0$ because energy is required to break the N–N bond.

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Reaction A: $4\ HCl(g) + O_2(g) \rightleftarrows 2\ Cl_2(g) + 2\ H_2O(g)$

Reaction B: $N_2O_4(g) \rightleftarrows 2\ NO_2(g)$

Reaction C: $H_2(g) + I_2(g) \rightleftarrows 2\ HI(g)$

Reaction D: $2\ NH_3(g) \rightleftarrows N_2(g) + 3\ H_2(g)$

26. The reactions represented above are carried out in sealed, rigid containers and allowed to reach equilibrium. If the volume of each container is reduced from 1.0 L to 0.5 L at constant temperature, for which of the reactions will the amount of product(s) be increased?

(A) Reaction A
(B) Reaction B
(C) Reaction C
(D) Reaction D

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Type of Steel	% Carbon	Characteristics	Uses
Low-carbon steel	< 0.2 %	Malleable and ductile	Chains and nails
High-carbon steel	0.6 – 1.5 %	Hard and brittle	Cutting tools

27. The table above provides some information about two types of steel, both of which are alloys of iron and carbon. Which of the following best helps to explain why high-carbon steel is more rigid than low-carbon steel?

(A) Elemental carbon is harder than elemental iron.
(B) The additional carbon atoms within the alloy make the high-carbon steel less dense.
(C) The additional carbon atoms within the alloy increase the thermal conductivity of the high-carbon steel.
(D) The additional carbon atoms within the alloy make it more difficult for the iron atoms to slide past one another.

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$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

28. The reaction between $NO_2(g)$ and $CO(g)$ is represented above. The elementary steps of a proposed reaction mechanism are represented below.

Step 1: $2\ NO_2(g) \rightarrow NO(g) + NO_3(g)$ (*slow*)

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (*fast*)

Which of the following is the rate law for the overall reaction that is consistent with the proposed mechanism?

(A) Rate = $k\ [NO_2][CO]$

(B) Rate = $k\ [NO_2]^2$

(C) Rate = $k\ [NO_3][CO]$

(D) Rate = $k\ [NO_2][NO_3][CO]$

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$$Cl^-(aq) + ClO^-(aq) + 2\ H^+(aq) \rightarrow Cl_2(g) + H_2O(l)$$

29. What effect will increasing $[H^+]$ at constant temperature have on the reaction represented above?

(A) The activation energy of the reaction will increase.
(B) The activation energy of the reaction will decrease.
(C) The frequency of collisions between Ht (aq) ions and $ClO^-(aq)$ ions will increase.
(D) The value of the rate constant will increase.

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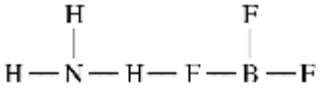
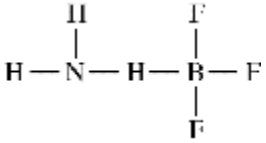
30. NH_3 reacts with BF_3 to form a single species. Which of the following structural diagrams is the most likely representation of the product of the reaction?

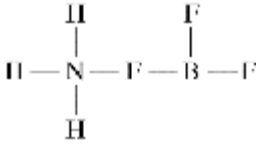
(A)



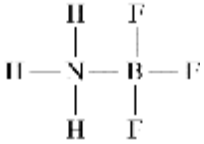
(B)



(C)



(D)



Half-Reaction	E° (V)
$Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$	– 2.37
$Cr^{3+}(aq) + 3\ e^- \rightarrow Cr(s)$	– 0.74

31. Based on the information in the table above, which of the following shows the cell potential and the Gibbs free energy change for the overall reaction that occurs in a standard galvanic cell?

	E°_{cell} (V)	ΔG° (kJ/mol$_{rxn}$)
(A)	+1.63	–157
(B)	+1.63	–944
(C)	+5.63	–543
(D)	+5.63	–3262

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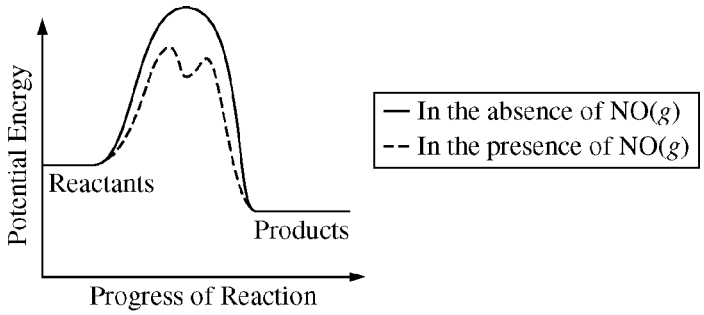
$$O_3(g) + O(g) \rightarrow 2\,O_2(g)$$

32. The decomposition of Oz(g) in the upper atmosphere is represented by the equation above. The potential energy diagram for the decomposition of $O_3(g)$ in the presence and absence of $NO(g)$ is given below.



Which of the following mechanisms for the catalyzed reaction is consistent with the equation and diagram above?

(A) $2\,O_3(g) + 2\,NO(g) \rightarrow 4\,O_2(g) + N_2(g)$ *slow*

(B) $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$ *slow*
$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$ *fast*

(C) $NO_2(g) + O_3(g) \rightarrow NO(g) + 2\,O_2(g)$ *slow*
$NO(g) + O(g) \rightarrow NO_2(g)$ *fast*

(D) $NO_2(g) + O(g) \rightarrow NO_3(g)$ *slow*
$NO_3(g) + O_3(g) \rightarrow NO_2(g) + 2\,O_2(g)$ *fast*

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$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + 3\ H_2O(l) \rightleftarrows 2\ \underset{\text{yellow}}{CrO_4^{2-}(aq)} + 2\ H_3O^+(aq)$$

33. The equilibrium system represented by the equation above initially contains equal concentrations of $Cr_2O_7^{2-}(aq)$ and $CrO_4^{2-}(aq)$. Which of the following statements correctly predicts the result of adding a sample of 6.0 *M* $NaOH(aq)$ to the system, and provides an explanation?

(A) The mixture will become more orange because $OH^-(aq)$ will oxidize the Cr in $CrO_4^{2-}(aq)$.

(B) The mixture will become more yellow because $OH^-(aq)$ will reduce the Cr in $Cr_2O_7^{2-}(aq)$.

(C) The mixture will become more yellow because $OH^-(aq)$ will shift the equilibrium toward products.

(D) The color of the mixture will not change because $OH^-(aq)$ does not appear in the equilibrium expression.

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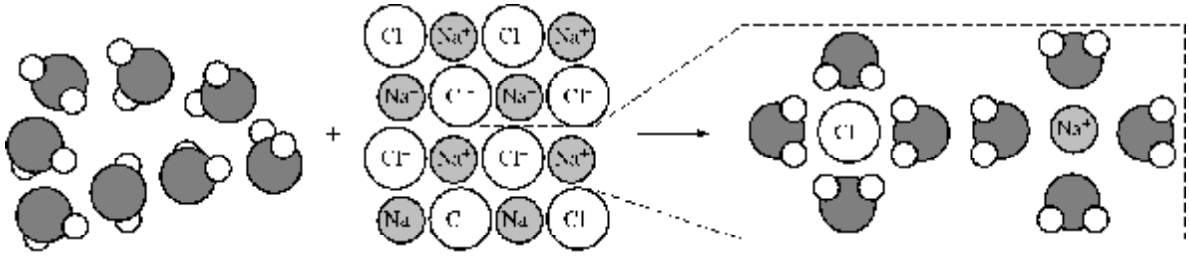

34. The process of dissolution of NaCl(s) in $H_2O(l)$ is represented in the diagram above. Which of the following summarizes the signs of $\Delta H°$ and $\Delta S°$ for each part of the dissolution process?

	Breaking solvent-solvent interactions		Breaking solute-solute interactions		Forming solute-solvent interactions	
	$\Delta H°$	$\Delta S°$	$\Delta H°$	$\Delta S°$	$\Delta H°$	$\Delta S°$
(A)	+	+	+	+	–	–
(B)	+	+	+	+	–	+
(C)	–	–	–	–	+	+
(D)	–	+	–	+	+	–

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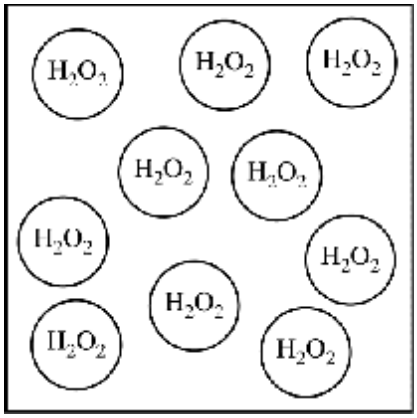
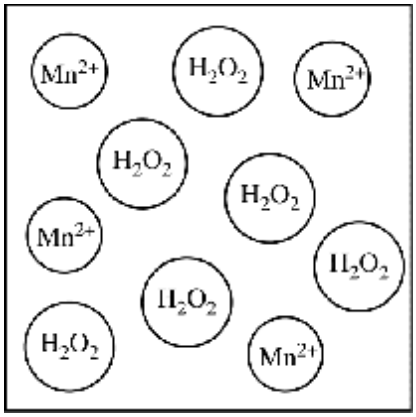


35. A particle view of a sample of $H_2O_2(aq)$ is shown above. The $H_2O_2(aq)$ is titrated with $KMnO_4(aq)$, as represented by the equation below.

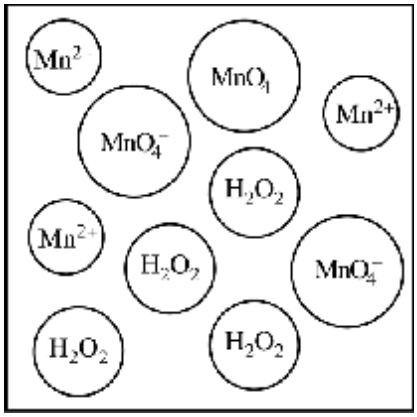
$$2\ MnO_4^-(aq) + 5\ H_2O_2(aq) + 6\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 5\ O_2(g) + 8\ H_2O(l)$$

Which of the following particle views best represents the mixture when the titration is halfway to the equivalence point? (H_2O molecules and H^+ ions are not shown.)

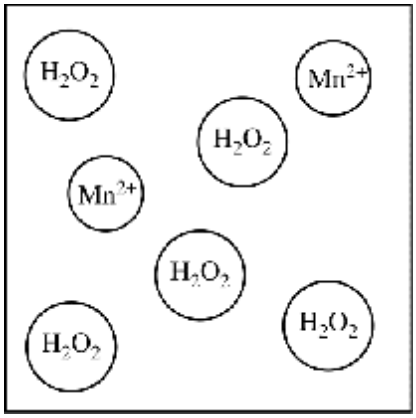
(A)



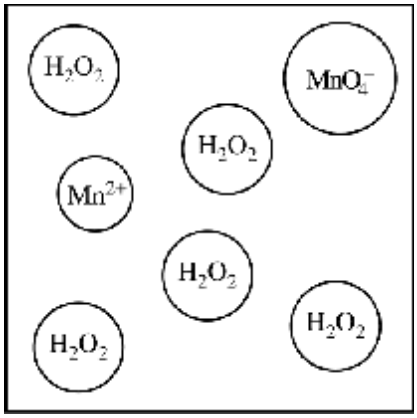
(B)



(C)



(D)



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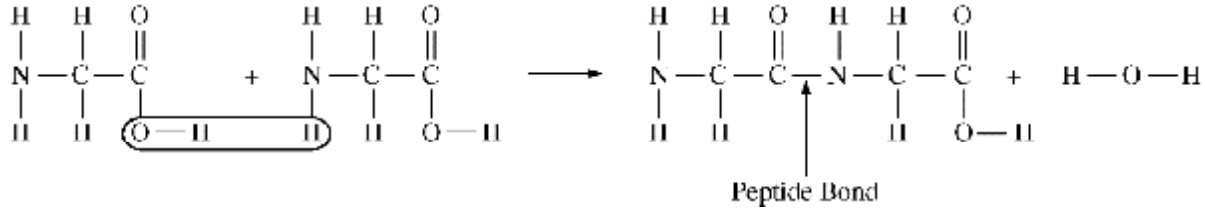
Questions 36-38 refer to the following information.



Two molecules of the amino acid glycine join through the formation of a peptide bond, as shown above. The thermodynamic data for the reaction are listed in the following table.

ΔG°_{298}	ΔH°_{298}	ΔS°_{298}
+15 kJ/mol$_{rxn}$	+12 kJ/mol$_{rxn}$	−10 J/(K·mol$_{rxn}$)

36. Under which of the following temperature conditions is the reaction thermodynamically favored?

(A) It is only favored at high temperatures.
(B) It is only favored at low temperatures.
(C) It is favored at all temperatures.
(D) It is not favored at any temperature.

Bond	Bond Energy (kJ/mol)
C–O	360
N–H	390
O–H	460

37. Based on the bond energies listed in the table above, which of the following is closest to the bond energy of the C–N bond?

(A) 200 kJ/mol
(B) 300 kJ/mol
(C) 400 kJ/mol
(D) 500 kJ/mol

38. Based on the thermodynamic data, which of the following is true at 298 K?

(A) $K_{eq} = 0$
(B) $0 < K_{eq} < 1$
(C) $K_{eq} = 1$
(D) $K_{eq} > 1$

Solution	Solute	K_{sp} at 25°C
X	AgBr	5.0×10^{-13}
Y	AgCl	1.8×10^{-10}
Z	AgI	8.3×10^{-17}

39. Three saturated solutions (X, Y, and Z) are prepared at 25°C. Based on the information in the table above, which of the following lists the solutions in order of increasing $[Ag^+]$?

(A) X < Z < Y
(B) Y < X < Z
(C) Z < Y < X
(D) Z < X < Y

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40. When 5.0 g of $NH_4ClO_4(s)$ is added to 100. mL of water in a calorimeter, the temperature of the solution formed decreases by 3.0°C. If 5.0 g of $NH_4ClO_4(s)$ is added to 1000. mL of water in a calorimeter initially at 25.0°C, the final temperature of the solution will be approximately

(A) 22.0°C
(B) 24.7°C
(C) 25.3°C
(D) 28.0°C

$$3\ O_2(g) \rightleftarrows 2\ O_3(g) \qquad K_c = 1.8 \times 10^{-56} \text{ at } 570\ K$$

41. For the system represented above, $[O_2]$ and $[O_3]$ initially are 0.150 mol/L and 2.5 mol/L respectively. Which of the following best predicts what will occur as the system approaches equilibrium at 570 K?

(A) The amount of $O_3(g)$ will increase, because $Q < K_c$.
(B) The amount of $O_3(g)$ will decrease, because $Q < K_c$.
(C) The amount of $O_3(g)$ will increase, because $Q > K_c$.
(D) The amount of $O_3(g)$ will decrease, because $Q > K_c$.

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Questions 42-43 refer to the following.

$$H_2(g) + Cl_2(g) \rightleftarrows 2\,HCl(g) \qquad K_p = 2 \times 10^{30} \text{ at } 298 \text{ K}$$

$HCl(g)$ can be synthesized from $H_2(g)$ and $Cl_2(g)$ as represented above. A student studying the kinetics of the reaction proposes the following mechanism.

Step 1: $Cl_2(g) \rightarrow 2\,Cl(g)$	(*slow*)	$\Delta H^\circ = 242 \text{ kJ/mol}_{rxn}$
Step 2: $H_2(g) + Cl(g) \rightarrow HCl(g) + H(g)$	(*fast*)	$\Delta H^\circ = 4 \text{ kJ/mol}_{rxn}$
Step 3: $H(g) + Cl(g) \rightarrow HCl(g)$	(*fast*)	$\Delta H^\circ = -432 \text{ kJ/mol}_{rxn}$

42. Which of the following statements identifies the greatest single reason that the value of K_p for the overall reaction at 298 K has such a large magnitude?

(A) The activation energy for step 1 of the mechanism is large and positive.
(B) The activation energy for step 2 of the mechanism is small and positive.
(C) The value of ΔS° for the overall reaction is small and positive.
(D) The value of ΔH° for the overall reaction is large and negative.

43. What is the value of the enthalpy change per mole of $HCl(g)$ produced?

(A) −93 kJ
(B) −121 kJ
(C) −186 kJ
(D) −242 kJ

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44. The compound CCl_4 is nonflammable and was once commonly used in fire extinguishers. On the basis of the periodic properties, which of the following compounds can most likely be used as a fire-resistant chemical?

(A) BCl_3
(B) CH_4
(C) CBr_4
(D) $PbCl_2$

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Reaction	K_{eq}
$La^{3+} + OH^- + HCO_3^- \rightleftarrows LaCO_3^+ + H_2O$	K_1
$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	K_a
$H_2O \rightleftarrows H^+ + OH^-$	K_w

45. Based on the information above, which of the following expressions represents the equilibrium constant, K, for the reaction represented by the equation below?

$$La^{3+} + CO_3^{2-} \rightleftarrows LaCO_3^+$$

(A) $K = (K_1)(K_a)(K_w)$

(B) $K = \dfrac{(K_1)(K_a)}{K_w}$

(C) $K = \dfrac{K_1}{(K_a)(K_w)}$

(D) $K = \dfrac{(K_1)(K_w)}{K_a}$

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$$ClO_2^-(aq) + HCOOH(aq) \rightleftarrows HClO_2(aq) + HCOO^-(aq) \qquad K_{eq} < 1$$

46. What are the relative strengths of the acids and bases in the reaction represented by the equation above?

	Acid Strength	Base Strength
(A)	$HClO_2 < HCOOH$	$ClO_2^- < HCOO^-$
(B)	$HClO_2 < HCOOH$	$ClO_2^- > HCOO^-$
(C)	$HClO_2 > HCOOH$	$ClO_2^- > HCOO^-$
(D)	$HClO_2 > HCOOH$	$ClO_2^- < HCOO^-$

$$Ag^+(aq) + NH_3(aq) \rightleftarrows Ag(NH_3)^+(aq) \qquad K_{eq_1} = 2.0 \times 10^3$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq) \qquad K_{eq_2} = 8.0 \times 10^3$$

47. Equal volumes of 0.1 *M* $AgNO_3(aq)$ and 2.0 *M* $NH_3(aq)$ are mixed and the reactions represented above occur. Which Ag species will have the highest concentration in the equilibrium system shown below, and why?

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq) \qquad K_{eq_3} = ?$$

(A) $Ag^+(aq)$, because $K_{eq_3} = 4$

(B) $Ag^+(aq)$, because $K_{eq_1} < K_{eq_2}$

(C) $Ag(NH_3)_2^+(aq)$, because $K_{eq_3} = 1.6 \times 10^7$

(D) $Ag(NH_3)_2^+(aq)$, because $K_{eq_1} < K_{eq_2}$

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

48. When $H_2(g)$ and $O_2(g)$ are mixed together in a rigid reaction vessel at 25°C, no reaction occurs. When the mixture is sparked, however, the gases react vigorously according to the equation above, releasing heat. Which of the following statements correctly explains why the spark is needed for the reaction to occur when the gases are originally at 25°C?

(A) The reaction is not thermodynamically favorable at 25°C.

(B) ΔH° for the reaction has a large positive value at 25°C.

(C) ΔS° for the reaction has a large negative value at 25°C.

(D) The reaction has a large activation energy at 25°C.

49. A student prepares a solution by combining 100 mL of 0.30 *M* $HNO_2(aq)$ and 100 mL of 0.30 *M* $KNO_2(aq)$. Which of the following equations represents the reaction that best helps to explain why adding a few drops of 1.0 *M* $HCl(aq)$ does not significantly change the pH of the solution?

(A) $K^+(aq) + Cl^-(aq) \rightarrow KCl(s)$

(B) $HNO_2(aq) \rightarrow H^+(aq) + NO_2^-(aq)$

(C) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

(D) $H^+(aq) + NO_2^-(aq) \rightarrow HNO_2(aq)$

$$2\ H_2O_2(l) \rightarrow 2\ H_2O(l) + O_2(g)$$

50. The exothermic process represented above is best classified as a

(A) physical change because a new phase appears in the products

(B) physical change because $O_2(g)$ that was dissolved comes out of solution

(C) chemical change because entropy increases as the process proceeds

(D) chemical change because covalent bonds are broken and new covalent bonds are formed

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CHEMISTRY

Section II

7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: 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.

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.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + C_2H_3O_2^-(aq)$$

1. The dissociation of ethanoic acid, $HC_2H_3O_2(aq)$, is represented above. A student is given the task of determining the value of K_a for $HC_2H_3O_2(aq)$ using two different experimental procedures.

   (a) The student is first asked to prepare 100.0 mL of 0.115 *M* $HC_2H_3O_2(aq)$ using a 2.000 *M* standard solution.

   (i) Calculate the volume, in mL, of 2.000 *M* $HC_2H_3O_2(aq)$ the student needs to prepare 100.0 mL of 0.115 *M* $HC_2H_3O_2(aq)$.

   (ii) Describe the procedure the student should use to prepare 100.0 mL of 0.115 *M* $HC_2H_3O_2(aq)$ using appropriate equipment selected from the list below. Assume that the student uses appropriate safety equipment.

   - 100 mL beaker
   - 100 mL graduated cylinder
   - 100 mL volumetric flask
   - Eye dropper
   - 500 mL wash bottle filled with distilled water
   - 2.000 *M* $HC_2H_3O_2(aq)$ in a 50 mL buret

   (b) Using a pH probe, the student determines that the pH of 0.115 *M* $HC_2H_3O_2(aq)$ is 2.92.

   (i) Using the pH value, calculate the value of K_a for $HC_2H_3O_2(aq)$.

   (ii) Calculate the percent dissociation of ethanoic acid in 0.115 *M* $HC_2H_3O_2(aq)$.

   In a separate experimental procedure, the student titrates 10.0 mL of the 2.000 *M* $HC_2H_3O_2(aq)$ with an $NaOH(aq)$ solution of unknown concentration. The student monitors the pH during the titration. The following titration curve was created using the experimental data presented in the table.

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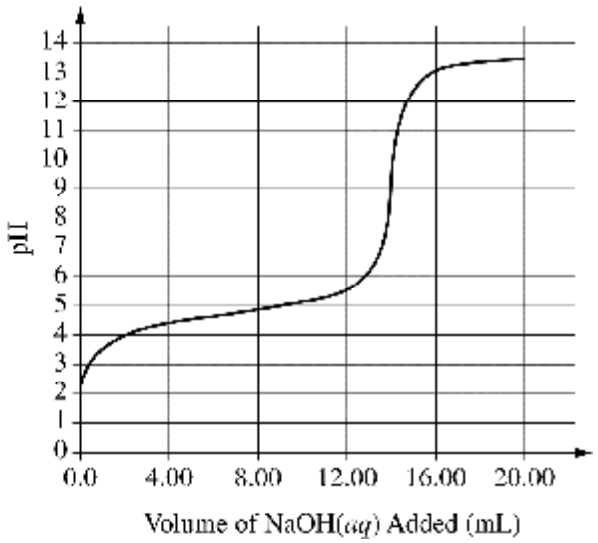
Volume of NaOH(*aq*) Added (mL)	pH
0.00	2.23
2.00	3.99
4.00	4.37
6.00	4.65
8.00	4.90
10.00	5.17
12.00	5.55
14.00	9.35
16.00	13.04
18.00	13.31
20.00	13.46



(c) Write the balanced net ionic equation for the reaction that occurs when $HC_2H_3O_2(aq)$ and NaOH(aq) are combined.

(d) Calculate the molar concentration of the NaOH(aq) solution.

(e) Explain how the student can estimate the value of K_a for $HC_2H_3O_2(aq)$ using the titration curve.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

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$$H_2O_2(aq) + OCl^-(aq) \rightarrow H_2O(l) + Cl^-(aq) + O_2(g)$$

2. A student investigates the reaction between $H_2O_2(aq)$ and $NaOCl(aq)$, which is represented by the net-ionic equation shown above.

(a) Is the reaction represented above a redox reaction? Justify your answer.

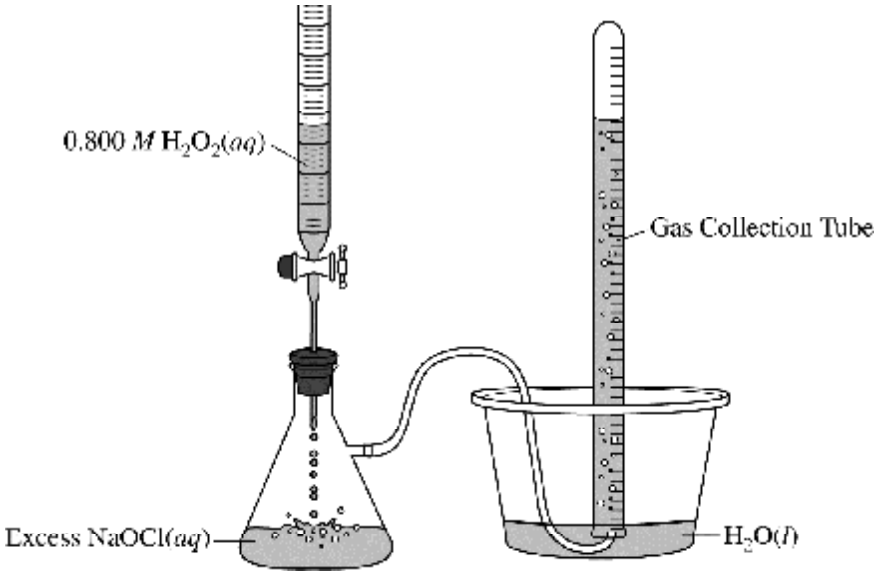
To better understand the reaction, the student looks up thermodynamic data for the reaction. For the reaction represented above, the value of ΔG°_{298} is -197 kJ/mol$_{rxn}$ and the value of ΔS°_{298} is 144 J/(K·mol$_{rxn}$).

(b) Calculate the value of ΔH°_{298} for the reaction in kJ/mol$_{rxn}$.

(c) Does the temperature inside the flask increase, decrease, or remain the same as the reaction proceeds? Justify your answer.

(d) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

The student decides to produce 40.0 mL of $O_2(g)$ at a pressure of 0.988 atm and a temperature of 298 K using the reaction represented above. The student uses the equipment shown below. The student sets up a 250 mL Erlenmeyer flask fitted with a one-hole stopper. The flask is connected to a 50 mL gas-collection tube that initially is completely filled with water.



(e) Calculate the volume of 0.800 M $H_2O_2(aq)$ that the student should add to excess $NaOCl(aq)$ to produce 40.0 mL of $O_2(g)$ at 0.988 atm and 298 K.

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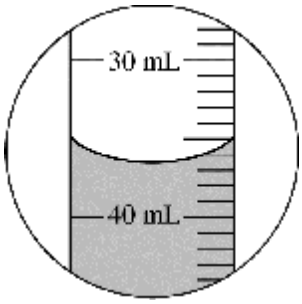
(f) The student added the amount of $H_2O_2(aq)$ calculated in part (e) to excess $NaOCl(aq)$. However, instead of producing 40.0 mL of $O_2(g)$, the volume indicated in the diagram below was produced.



(i) Based on the diagram above, what volume of gas was produced?

(ii) Assuming that all the gas in the tube is $O_2(g)$, calculate the percent yield of $O_2(g)$.

(iii) Is the assumption that all the gas in the tube is $O_2(g)$ correct? Explain.

(g) To account for the percent yield being less than 100 percent, the student claims that the reaction reached equilibrium before the expected amount of $O_2(g)$ was produced. Considering your answer to part (d) above, do you agree or disagree with the student's claim? Justify your answer.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

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3. Answer the following questions about ozone.

(a) The O_3 molecule has a central oxygen atom bonded to two outer oxygen atoms that are not bonded to one another. In the box below, draw the Lewis electron-dot diagram of the Oz molecule. Include all valid resonance structures.

(b) Based on the diagram you drew in part (a), what is the shape of the ozone molecule?

Ozone decomposes according to the reaction represented below.

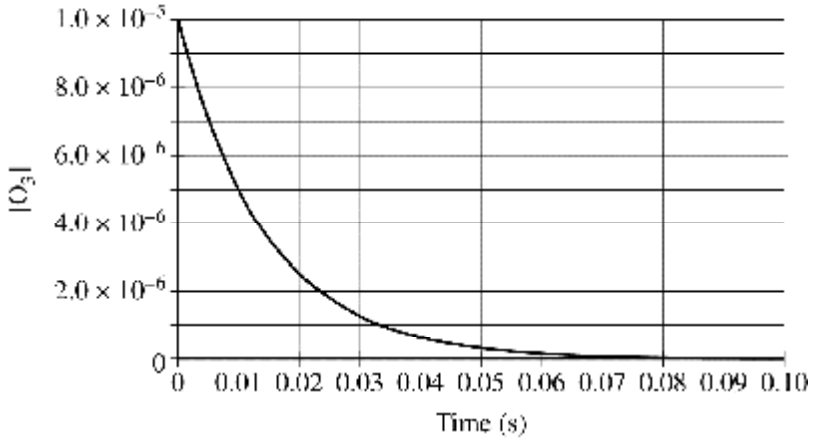
$$2\ O_3(g) \rightarrow 3\ O_2(g) \qquad \Delta H^\circ = -285\ \text{kJ/mol}_{rxn}$$

(c) The bond enthalpy of the oxygen-oxygen bond in O_2 is 498 kJ/mol. Based on the enthalpy of the reaction represented above, what is the average bond enthalpy, in kJ/mol, of an oxygen-oxygen bond in O_3 ?

Ozone can oxidize $HSO_3^-(aq)$, as represented by the equation below.

$$HSO_3^-(aq) + O_3(aq) \rightarrow HSO_4^-(aq) + O_2(g)$$

A solution is prepared in which the initial concentration of $HSO_3^-(aq)$ $(6.4 \times 10^{-4}\ M)$ is much larger than that of $O_3(aq)$ $(1.0 \times 10^{-5}\ M)$. The concentration of $O_3(aq)$ is monitored as the reaction proceeds, and the data are plotted in the graph below.



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(d) The data are consistent with the following rate law: rate = $k_1[O_3]$.

(i) Based on the graph on the previous page, determine the half-life of the reaction.

(ii) Determine the value of the rate constant, ky, for the rate law. Include units with your answer.

(iii) Considering the relative concentrations of the reactants, briefly explain why the data in the graph are also consistent with the following rate law: rate = $k_2[O_3][HSO_3^-]$.

(iv) Briefly describe an experiment that could provide evidence to support the rate law given in part (d)(ili).

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

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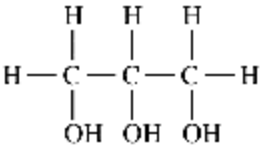
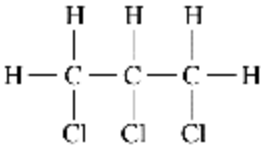


Glycerol

Boiling point 290°C



Trichloropropane

Boiling point 157°C

4. The structural formulas of glycerol and trichloropropane are given above. Both compounds are liquids at 25°C.

   (a) For each compound, identify all types of intermolecular forces present in the liquid. Explain why glycerol has the higher boiling point in terms of the relative strengths of the intermolecular forces.

   (b) Glycerol (molar mass 92.09 g/mol) has been suggested for use as an alternative fuel. The enthalpy of combustion, ΔH°_{comb}, of glycerol is −1654 kJ/mol. What mass of glycerol would need to be combusted to heat 500.0 g of water from 20.0°C to 100.0°C ? (The specific heat capacity of water is 4.184 J/(g · °C). Assume that all the heat released by the combustion reaction is absorbed by the water.)

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ADDITIONAL PAGE FOR ANSWERING QUESTION 4

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Overall reaction: $Pb(s) + PbO_2(s) + 2\ H^+(aq) + 2\ HSO_4^-(aq) \rightarrow 2\ PbSO_4(s) + 2\ H_2O(l)$

Cathode half-cell reaction: $PbO_2(s) + 3\ H^+(aq) + HSO_4^-(aq) + 2\ e^- \rightarrow PbSO_4(s) + 2\ H_2O(l)$

5. The equations above represent reactions associated with the operation of a lead storage battery. The first is the overall reaction that occurs as the battery produces an electrical current, and the second is the half-reaction that occurs at the cathode.

(a) Determine the oxidation number of sulfur in the overall reaction.

(b) Write the equation for the half-reaction that occurs at the anode as the battery operates.

After the battery has operated for some time, it can be recharged by applying a current to reverse the overall reaction.

(c) Calculate the time, in seconds, needed to regenerate 100. g of $Pb(s)$ in the battery by applying a current of 5.00 amp.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 5

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6. Answer the following questions about the solubility of $AgCl(s)$. The value of K_{sp} for $AgCl(s)$ is 1.8×10^{-10}.

(a) Calculate the value of $[Ag^+]$ in a saturated solution of $AgCl$ in distilled water.

(b) The concentration of $Cl^-(aq)$ in seawater is $0.54\ M$.

(i) Calculate the molar solubility of $AgCl(s)$ in seawater.

(ii) Explain why $AgCl(s)$ is less soluble in seawater than in distilled water.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 6

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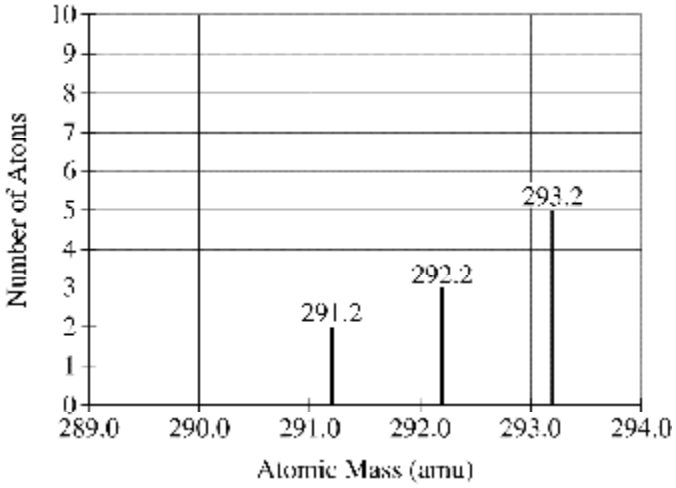
7. A new element with atomic number 116 was discovered in 2000. In 2012 it was named livermorium, Lv. Although Lv is radioactive and short-lived, its chemical properties and reactivity should follow periodic trends.

(a) Write the electron configuration for the valence electrons of Lv in the ground state.

(b) According to periodic properties, what would be the most likely formula for the product obtained when Lv reacts with $H_2(g)$?

(c) The first ionization energy of polonium, Po, is 812 kJ/mol. Is the first ionization energy of Lv expected to be greater than, less than, or equal to that of Po? Justify your answer in terms of Coulomb's law.

(d) Shown below is a hypothetical mass spectrum for a sample of Lv containing 10 atoms.



Using the information in the graph, determine the average atomic mass of Lv in the sample to four significant figures.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 7

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DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1												13	14	15	16	17	18
1 **H** 1.008	2																2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30	3	4	5	6	7	8	9	10	11	12	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (97)	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 ***La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **†Ac** (227)	104 **Rf** (267)	105 **Db** (270)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (282)	112 **Cn** (285)	113 **Uut** (285)	114 **Fl** (289)	115 **Uup** (288)	116 **Lv** (293)	117 **Uus** (294)	118 **Uuo** (294)

*Lanthanoid Series	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.05	71 **Lu** 174.97
†Actinoid Series	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

AP® CHEMISTRY EQUATIONS AND CONSTANTS

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

L, mL	=	liter(s), milliliter(s)	mm Hg	=	millimeters of mercury
g	=	gram(s)	J, kJ	=	joule(s), kilojoule(s)
nm	=	nanometer(s)	V	=	volt(s)
atm	=	atmosphere(s)	mol	=	mole(s)

ATOMIC STRUCTURE

$E = h\nu$

$c = \lambda\nu$

E = energy
ν = frequency
λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s
Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}
Avogadro's number = 6.022×10^{23} mol^{-1}
Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$, where $a\,A + b\,B \rightleftarrows c\,C + d\,D$

$K_p = \dfrac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$

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

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

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

$= K_a \times K_b$

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

$14 = pH + pOH$

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

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

Equilibrium Constants

K_c (molar concentrations)
K_p (gas pressures)
K_a (weak acid)
K_b (weak base)
K_w (water)

KINETICS

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

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

$t_{1/2} = \dfrac{0.693}{k}$

k = rate constant
t = time
$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

$$\text{K} = \text{°C} + 273$$

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

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

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
$\boldsymbol{M}$ = molar mass
D = density
KE = kinetic energy
v = velocity
A = absorbance
a = molar absorptivity
b = path length
c = concentration

Gas constant, R = 8.314 J mol^{-1} K^{-1}
= 0.08206 L atm mol^{-1} K^{-1}
= 62.36 L torr mol^{-1} K^{-1}
1 atm = 760 mm Hg = 760 torr
STP = 273.15 K and 1.0 atm
Ideal gas at STP = 22.4 L mol^{-1}

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

$$\Delta G° = \Delta H° - T\Delta S°$$
$$= -RT \ln K$$
$$= -nFE°$$

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

q = heat
m = mass
c = specific heat capacity
T = temperature
$S°$ = standard entropy
$H°$ = standard enthalpy
$G°$ = standard Gibbs free energy
n = number of moles
$E°$ = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$