

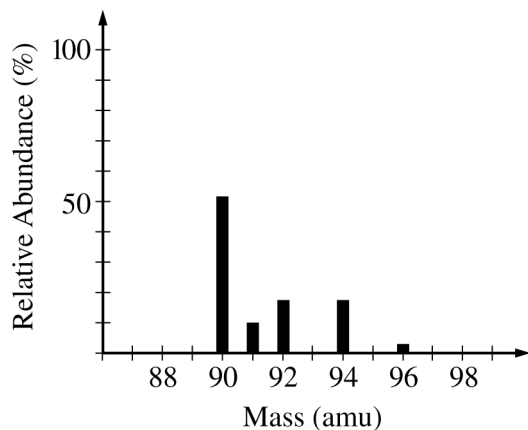
CHEMISTRY
Section I
50 Questions
Time—90 minutes

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.

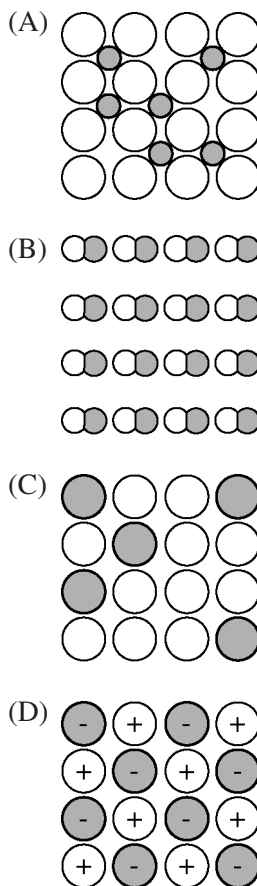
Directions: Each of the questions or incomplete statements below is followed by four suggested answers or completions. Select the one that is best in each case and then fill in the corresponding circle on the answer sheet.

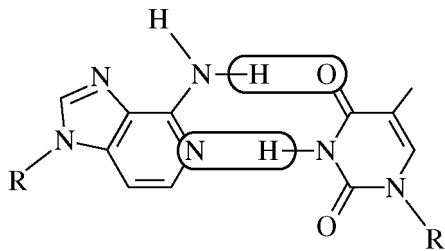
1. A 0.5 mol sample of $\text{He}(g)$ and a 0.5 mol sample of $\text{Ne}(g)$ are placed separately in two 10.0 L rigid containers at 25°C . Each container has a pinhole opening. Which of the gases, $\text{He}(g)$ or $\text{Ne}(g)$, will escape faster through the pinhole and why?
 - (A) $\text{He}(g)$ will escape faster because the $\text{He}(g)$ atoms are moving at a higher average speed than the $\text{Ne}(g)$ atoms.
 - (B) $\text{Ne}(g)$ will escape faster because its initial pressure in the container is higher.
 - (C) $\text{Ne}(g)$ will escape faster because the $\text{Ne}(g)$ atoms have a higher average kinetic energy than the $\text{He}(g)$ atoms.
 - (D) Both gases will escape at the same rate because the atoms of both gases have the same average kinetic energy.
2. The lattice energy of a salt is related to the energy required to separate the ions. For which of the following pairs of ions is the energy that is required to separate the ions largest? (Assume that the distance between the ions in each pair is equal to the sum of the ionic radii.)
 - (A) $\text{Na}^+(g)$ and $\text{Cl}^-(g)$
 - (B) $\text{Cs}^+(g)$ and $\text{Br}^-(g)$
 - (C) $\text{Mg}^{2+}(g)$ and $\text{O}^{2-}(g)$
 - (D) $\text{Ca}^{2+}(g)$ and $\text{O}^{2-}(g)$



3. The mass spectrum of element X is presented in the diagram above. Based on the spectrum, which of the following can be concluded about element X?
- (A) X is a transition metal, and each peak represents an oxidation state of the metal.
 - (B) X contains five electron sublevels.
 - (C) The atomic mass of X is 90.
 - (D) The atomic mass of X is between 90 and 92.

4. Which of the following diagrams best depicts an alloy of Ni and B ?





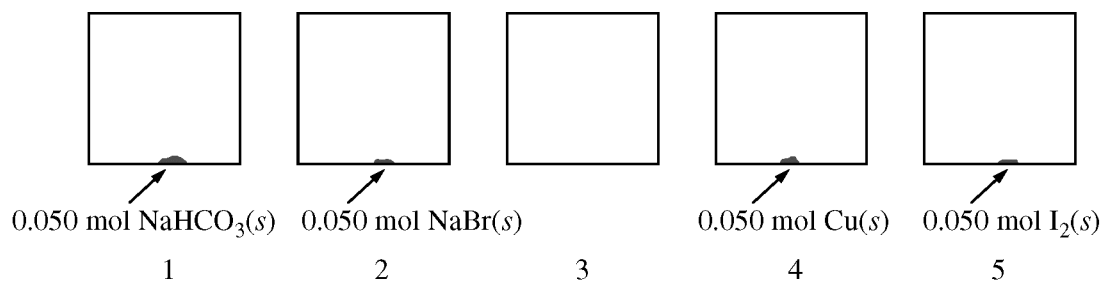
5. Which of the following is the strongest type of interaction that occurs between the atoms within the circled areas of the two molecules represented above?

(A) Polar covalent bond
 (B) Nonpolar covalent bond
 (C) Hydrogen bond
 (D) London dispersion forces

6. A hot iron ball is dropped into a 200. g sample of water initially at 50.°C. If 8.4 kJ of heat is transferred from the ball to the water, what is the final temperature of the water? (The specific heat of water is 4.2 J/(g·°C).)

(A) 40.°C
 (B) 51°C
 (C) 60.°C
 (D) 70.°C

Questions 7-9 refer to the following information.

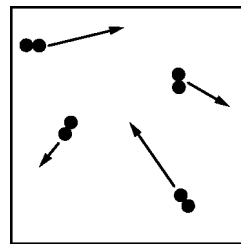


At 27°C , five identical rigid 2.0 L vessels are filled with $\text{N}_2(g)$ and sealed. Four of the five vessels also contain a 0.050 mol sample of $\text{NaHCO}_3(s)$, $\text{NaBr}(s)$, $\text{Cu}(s)$, or $\text{I}_2(s)$, as shown in the diagram above. The volume taken up by the solids is negligible, and the initial pressure of $\text{N}_2(g)$ in each vessel is 720 mm Hg. All four vessels are heated to 127°C and allowed to reach a constant pressure.

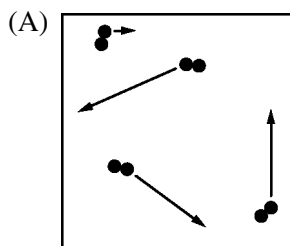
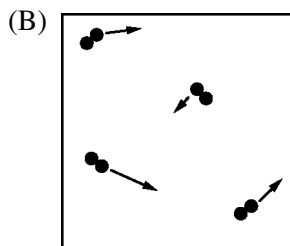
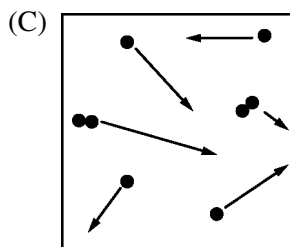
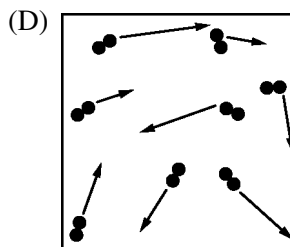
7. At 127°C , the pressure in vessel 1 is found to be higher than that in vessel 2. Which of the following reactions best accounts for the observation?
- (A) $\text{NaHCO}_3(s) \rightarrow \text{Na}(s) + \text{HCO}_3(s)$
- (B) $\text{NaHCO}_3(s) \rightarrow \text{NaH}(s) + \text{CO}_3(s)$
- (C) $2 \text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$
- (D) $2 \text{NaHCO}_3(s) + \text{N}_2(g) \rightarrow 2 \text{NaNO}_3(s) + \text{C}_2\text{H}_2(g)$

8. At 127°C , the entire sample of I_2 is observed to have vaporized. How does the mass of vessel 5 at 127°C compare to its mass at 27°C ?

- (A) The mass is less, since the I_2 is in the vapor phase.
- (B) The mass is the same, since the number of each type of atom in the vessel is constant.
- (C) The mass is greater, since the I_2 will react with N_2 to form NI_3 , which has a greater molar mass.
- (D) The mass is greater, since the pressure is greater and the particles have a higher average kinetic energy.



9. The gas particles in vessel 3 at 27°C are represented in the diagram above. The lengths of the arrows represent the speeds of the particles. Which of the following diagrams best represents the particles when vessel 3 is heated to 127°C ?



10. An acetate buffer solution is prepared by combining 50. mL of 0.20 *M* acetic acid, HC₂H₃O₂(*aq*), and 50. mL of 0.20 *M* sodium acetate, NaC₂H₃O₂(*aq*). A 5.0 mL sample of 0.10 *M* NaOH(*aq*) is added to the buffer solution. Which of the following is a correct pairing of the acetate species present in greater concentration and of the pH of the solution after the NaOH(*aq*) is added? (The *pK_a* of acetic acid is 4.7.)

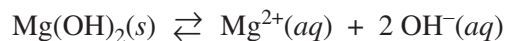
	Acetate Species	pH
(A)	HC ₂ H ₃ O ₂	< 4.7
(B)	HC ₂ H ₃ O ₂	> 4.7
(C)	C ₂ H ₃ O ₂ ⁻	< 4.7
(D)	C ₂ H ₃ O ₂ ⁻	> 4.7

Name	Molecular Formula	Molar Mass (g/mol)
Ethane	C ₂ H ₆	30
Butane	C ₄ H ₁₀	58

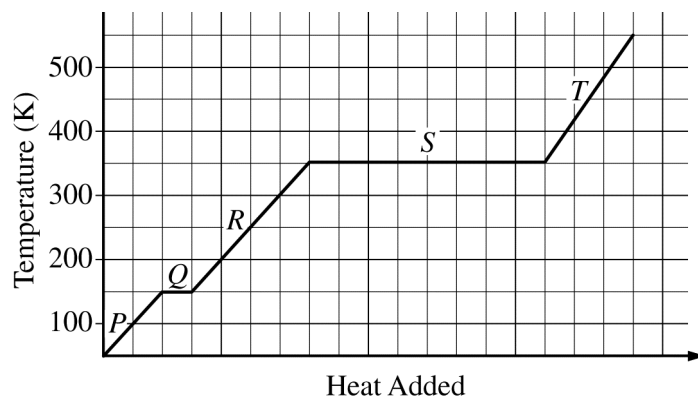
11. The molecular formula and molar mass of two straight-chain hydrocarbons are listed in the table above. Based on the information in the table, which compound has the higher boiling point, and why is that compound's boiling point higher?
- (A) C₄H₁₀, because it has more hydrogen atoms, resulting in more hydrogen bonding
- (B) C₄H₁₀, because it has more electrons, resulting in greater polarizability and stronger dispersion forces
- (C) C₂H₆, because its molecules are smaller and they can get closer to one another, resulting in stronger dispersion forces
- (D) C₂H₆, because its molecules are more polar, resulting in stronger dipole-dipole attractions

	Ionization Energy (kJ/mol)
First	801
Second	2,430
Third	3,660
Fourth	25,000
Fifth	32,820

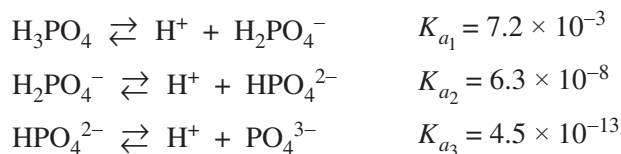
12. The first five ionization energies of a second-period element are listed in the table above. Which of the following correctly identifies the element and best explains the data in the table?
- (A) B, because it has five core electrons
- (B) B, because it has three valence electrons
- (C) N, because it has five valence electrons
- (D) N, because it has three electrons in the *p* sublevel



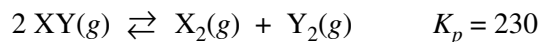
13. The exothermic dissolution of Mg(OH)₂(*s*) in water is represented by the equation above. The *K_{sp}* of Mg(OH)₂ is 1.8×10^{-11} . Which of the following changes will increase the solubility of Mg(OH)₂ in an aqueous solution?
- (A) Decreasing the pH
- (B) Increasing the pH
- (C) Adding NH₃ to the solution
- (D) Adding Mg(NO₃)₂ to the solution



14. The heating curve for a sample of pure ethanol is provided above. The temperature was recorded as a 50.0 g sample of solid ethanol was heated at a constant rate. Which of the following explains why the slope of segment *T* is greater than the slope of segment *R* ?
- (A) The specific heat capacity of the gaseous ethanol is less than the specific heat capacity of liquid ethanol.
 - (B) The specific heat capacity of the gaseous ethanol is greater than the specific heat capacity of liquid ethanol.
 - (C) The heat of vaporization of ethanol is less than the heat of fusion of ethanol.
 - (D) The heat of vaporization of ethanol is greater than the heat of fusion of ethanol.



15. A solution is prepared by mixing 50 mL of 1 *M* NaH₂PO₄ with 50 mL of 1 *M* Na₂HPO₄. On the basis of the information above, which of the following species is present in the solution at the lowest concentration?
- (A) Na⁺
 - (B) HPO₄²⁻
 - (C) H₂PO₄⁻
 - (D) PO₄³⁻



16. A certain gas, XY(g) , decomposes as represented by the equation above. A sample of each of the three gases is put in a previously evacuated container. The initial partial pressures of the gases are shown in the table below.

Gas	Initial Partial Pressure (atm)
XY	0.010
X_2	0.20
Y_2	2.0

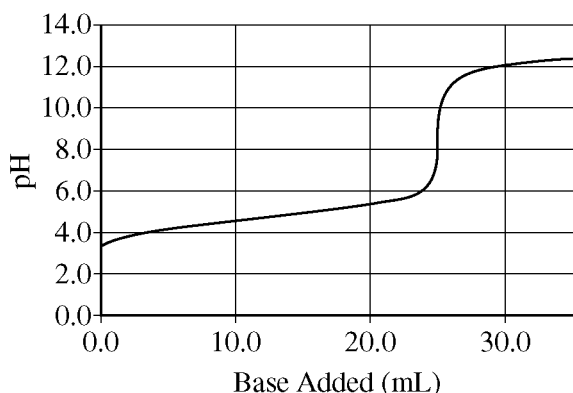
The temperature of the reaction mixture is held constant. In which direction will the reaction proceed?

- (A) The reaction will form more products.
 (B) The reaction will form more reactant.
 (C) The mixture is at equilibrium, so there will be no change.
 (D) It cannot be determined unless the volume of the container is known.

Questions 17-20 refer to the following information.

A 0.35 g sample of Li(s) is placed in an Erlenmeyer flask containing 100 mL of water at 25°C . A balloon is placed over the mouth of the flask to collect the hydrogen gas that is generated.

After all of the Li(s) has reacted with $\text{H}_2\text{O(l)}$, the solution in the flask is added to a clean, dry buret and used to titrate an aqueous solution of a monoprotic acid. The pH curve for this titration is shown in the diagram below.



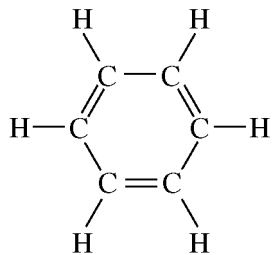
17. Which of the following changes will most likely increase the rate of reaction between Li(s) and water?
- (A) Using 125 mL of water instead of 100 mL
 (B) Using a 0.25 g sample of Li(s) instead of a 0.35 g sample
 (C) Using a 0.35 g sample of Li(s) cut into small pieces
 (D) Decreasing the water temperature before adding the Li(s)
18. What will be the effect on the amount of gas produced if the experiment is repeated using 0.35 g of K(s) instead of 0.35 g of Li(s) ?
- (A) No gas will be produced when K(s) is used.
 (B) Some gas will be produced but less than the amount of gas produced with Li(s) .
 (C) Equal quantities of gas will be produced with the two metals.
 (D) More gas will be produced with K(s) than with Li(s) .

19. On the basis of the pH curve, the pK_a value of the acid is closest to

- (A) 4
- (B) 5
- (C) 8
- (D) 12

20. Which of the following is the balanced net-ionic equation for the reaction between $\text{Li}(s)$ and water?

- (A) $2 \text{Li}(s) + 2 \text{H}^+(aq) + 2 \text{OH}^-(aq) \rightarrow 2 \text{Li}^+(aq) + 2 \text{OH}^-(aq) + \text{H}_2(g)$
- (B) $2 \text{Li}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Li}^+(aq) + 2 \text{OH}^-(aq) + \text{H}_2(g)$
- (C) $2 \text{Li}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{LiOH}(s) + \text{H}_2(g)$
- (D) $2 \text{Li}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{LiH}(s) + \text{H}_2(g)$

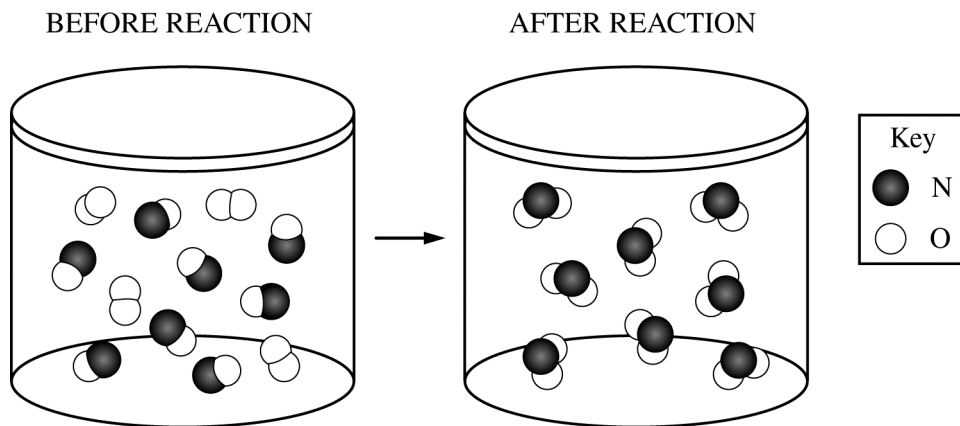


21. Benzene, C_6H_6 , has the structure shown above. Considering the observation that benzene is only sparingly soluble in water, which of the following best describes the intermolecular forces of attraction between water and benzene?
- (A) Benzene is nonpolar, therefore there are no forces between water and benzene.
 (B) The H atoms in benzene form hydrogen bonds with the O atoms in water.
 (C) Benzene is hydrophobic, therefore there is a net repulsion between water and benzene.
 (D) There are dipole-induced dipole and London dispersion interactions between water and benzene.

Solution	Acid	K_a
1	CH_3CO_2H	1.75×10^{-5}
2	CF_3CO_2H	1.0×10^0

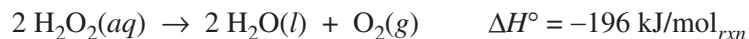
22. Acid-dissociation constants of two acids are listed in the table above. A 20. mL sample of a 0.10 M solution of each acid is titrated to the equivalence point with 20. mL of 0.10 M NaOH. Which of the following is a true statement about the pH of the solutions at the equivalence point?
- (A) Solution 1 has a higher pH at the equivalence point because CH_3CO_2H is the stronger acid.
 (B) Solution 1 has a higher pH at the equivalence point because CH_3CO_2H has the stronger conjugate base.
 (C) Solution 1 has a lower pH at the equivalence point because CH_3CO_2H is the stronger acid.
 (D) Solution 1 has a lower pH at the equivalence point because CH_3CO_2H has the stronger conjugate base.

23. A 1.0 g sample of a cashew was burned in a calorimeter containing 1000. g of water, and the temperature of the water changed from 20.0°C to 25.0°C. In another experiment, a 3.0 g sample of a marshmallow was burned in a calorimeter containing 2000. g of water, and the temperature of the water changed from 25.0°C to 30.0°C. Based on the data, which of the following can be concluded about the energy content for 1.0 g of each of the two substances? (The specific heat of water is 4.2 J/(g·°C).)
- (A) The combustion of 1.0 g of cashew releases less energy than the combustion of 1.0 g of marshmallow.
 (B) The combustion of 1.0 g of cashew releases the same amount of energy as the combustion of 1.0 g of marshmallow.
 (C) The combustion of 1.0 g of cashew releases more energy than the combustion of 1.0 g of marshmallow.
 (D) No comparison can be made because the two systems started with different masses of food, different masses of water, and different initial temperatures.



24. The reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ to produce $\text{NO}_2(g)$ in a rigid reaction vessel is represented in the diagram above. The pressure inside the container is recorded using a pressure gauge. Which of the following statements correctly predicts the change in pressure as the reaction goes to completion at constant temperature, and provides the correct explanation?
- (A) The pressure will increase because the product molecules have a greater mass than either of the reactant molecules.
 - (B) The pressure will decrease because there are fewer molecules of product than of reactants.
 - (C) The pressure will decrease because the product molecules have a lower average speed than the reactant molecules.
 - (D) The pressure will not change because the total mass of the product molecules is the same as the total mass of the reactant molecules.

Questions 25-29 refer to the following information.



The decomposition of $\text{H}_2\text{O}_2(aq)$ is represented by the equation above. A student monitored the decomposition of a 1.0 L sample of $\text{H}_2\text{O}_2(aq)$ at a constant temperature of 300. K and recorded the concentration of H_2O_2 as a function of time. The results are given in the table below.

Time (s)	$[\text{H}_2\text{O}_2]$
0	2.7
200.	2.1
400.	1.7
600.	1.4

25. Which of the following identifies the element(s) being oxidized and reduced in the reaction?
- (A) Hydrogen is oxidized and oxygen is reduced.
(B) Oxygen is oxidized and hydrogen is reduced.
(C) Oxygen is both oxidized and reduced.
(D) No elements are oxidized or reduced; the reaction is not a redox reaction.
26. The $\text{O}_2(g)$ produced from the decomposition of the 1.0 L sample of $\text{H}_2\text{O}_2(aq)$ is collected in a previously evacuated 10.0 L flask at 300. K. What is the approximate pressure in the flask after 400. s? (For estimation purposes, assume that 1.0 mole of gas in 1.0 L exerts a pressure of 24 atm at 300. K.)
- (A) 1.2 atm
(B) 2.4 atm
(C) 12 atm
(D) 24 atm
27. Which of the following statements is a correct interpretation of the data regarding how the order of the reaction can be determined?
- (A) The reaction must be first order because there is only one reactant species.
(B) The reaction is first order if the plot of $\ln [\text{H}_2\text{O}_2]$ versus time is a straight line.
(C) The reaction is first order if the plot of $1/[\text{H}_2\text{O}_2]$ versus time is a straight line.
(D) The reaction is second order because 2 is the coefficient of H_2O_2 in the chemical equation.
28. The reaction is thermodynamically favorable. The signs of ΔG° and ΔS° for the reaction are which of the following?
- | | ΔG° | ΔS° |
|-----|------------------|------------------|
| (A) | Positive | Positive |
| (B) | Negative | Positive |
| (C) | Positive | Negative |
| (D) | Negative | Negative |

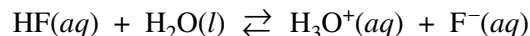
29. Assume that the bond enthalpies of the oxygen-hydrogen bonds in H_2O are not significantly different from those in H_2O_2 . Based on the value of ΔH° of the reaction, which of the following could be the bond enthalpies (in kJ/mol) for the bonds broken and formed in the reaction?

	O–O in H_2O_2	O=O in O_2	O–H
(A)	300	500	500
(B)	150	500	500
(C)	500	300	150
(D)	250	300	150

30. Which of the following accounts for the observation that the pH of pure water at 37°C is 6.8 ?
- (A) At 37°C water is naturally acidic.
- (B) At 37°C the autoionization constant for water, K_w , is larger than it is at 25°C .
- (C) At 37°C water has a lower density than it does at 25°C ; therefore, $[\text{H}^+]$ is greater.
- (D) At 37°C water ionizes to a lesser extent than it does at 25°C .
31. To gravimetrically analyze the silver content of a piece of jewelry made from an alloy of Ag and Cu, a student dissolves a small preweighed sample in $\text{HNO}_3(\text{aq})$. $\text{Ag}^+(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ ions form in the solution. Which of the following should be the next step in the analytical process?
- (A) Centrifuging the solution to isolate the heavier ions
- (B) Evaporating the solution to recover the dissolved nitrates
- (C) Adding enough base solution to bring the pH up to 7.0
- (D) Adding a solution containing an anion that forms an insoluble salt with only one of the metal ions

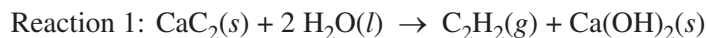
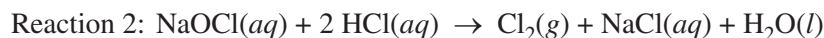
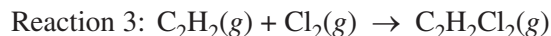
32. A sample of a compound that contains only the elements C, H, and N is completely burned in O_2 to produce 44.0 g of CO_2 , 45.0 g of H_2O , and some NO_2 . A possible empirical formula of the compound is

- (A) CH_2N
 (B) CH_5N
 (C) $\text{C}_2\text{H}_5\text{N}$
 (D) $\text{C}_3\text{H}_3\text{N}_2$



33. The dissociation of the weak acid HF in water is represented by the equation above. Adding a 1.0 mL sample of which of the following would increase the percent ionization of $\text{HF}(\text{aq})$ in 10 mL of a solution of 1.0 M HF ?
- (A) 1.0 M KF
- (B) 1.0 M H_2SO_4
- (C) 10.0 M HF
- (D) Distilled water

Questions 34-36 refer to the reactions represented below, which are involved in a demonstration commonly known as “underwater fireworks.”

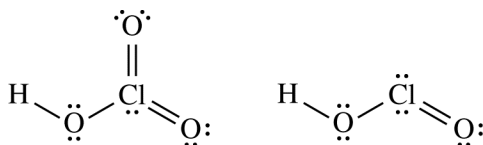


34. $\text{Ca}(\text{OH})_2(s)$ precipitates when a 1.0 g sample of $\text{CaC}_2(s)$ is added to 1.0 L of distilled water at room temperature. If a 0.064 g sample of $\text{CaC}_2(s)$ (molar mass 64 g/mol) is used instead and all of it reacts, which of the following will occur and why? (The value of K_{sp} for $\text{Ca}(\text{OH})_2$ is 8.0×10^{-8} .)
- (A) $\text{Ca}(\text{OH})_2$ will precipitate because $Q > K_{sp}$.
- (B) $\text{Ca}(\text{OH})_2$ will precipitate because $Q < K_{sp}$.
- (C) $\text{Ca}(\text{OH})_2$ will not precipitate because $Q > K_{sp}$.
- (D) $\text{Ca}(\text{OH})_2$ will not precipitate because $Q < K_{sp}$.
35. Reaction 2 occurs when an excess of 6 M $\text{HCl}(aq)$ solution is added to 100. mL of $\text{NaOCl}(aq)$ of unknown concentration. If the reaction goes to completion and 0.010 mol of $\text{Cl}_2(g)$ is produced, then what was the molarity of the $\text{NaOCl}(aq)$ solution?
- (A) 0.0010 M
- (B) 0.010 M
- (C) 0.10 M
- (D) 1.0 M
36. When Reaction 3 occurs, does the hybridization of the carbon atoms change?
- (A) Yes; it changes from sp to sp^2 .
- (B) Yes; it changes from sp to sp^3 .
- (C) Yes; it changes from sp^2 to sp^3 .
- (D) No; it does not change.

	K_a
$\text{HC}_3\text{H}_5\text{O}_3(aq)$	8.3×10^{-4}
$\text{CH}_3\text{NH}_3^+(aq)$	2.3×10^{-11}

37. The acid-dissociation constants of $\text{HC}_3\text{H}_5\text{O}_3(aq)$ and $\text{CH}_3\text{NH}_3^+(aq)$ are given in the table above. Which of the following mixtures is a buffer with a pH of approximately 3 ?

- (A) A mixture of 100. mL of 0.1 M $\text{CH}_3\text{NH}_3\text{Cl}$ and 50. mL of 0.1 M NaOH
 (B) A mixture of 100. mL of 0.1 M $\text{HC}_3\text{H}_5\text{O}_3$ and 50. mL of 0.1 M NaOH
 (C) A mixture of 100. mL of 0.1 M $\text{NaC}_3\text{H}_5\text{O}_3$ and 100. mL of 0.1 M NaOH
 (D) A mixture of 100. mL of 0.1 M $\text{CH}_3\text{NH}_3\text{Cl}$ and 100. mL of 0.1 M CH_3NH_2

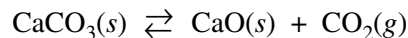


38. The Lewis electron-dot diagrams of the HClO_3 molecule and the HClO_2 molecule are shown above at the left and right, respectively. Which of the following statements identifies the stronger acid and correctly identifies a factor that contributes to its being the stronger acid?

- (A) $\text{HClO}_3(aq)$ is the stronger acid because its molecules experience stronger London dispersion forces.
 (B) $\text{HClO}_3(aq)$ is the stronger acid because the additional electronegative oxygen atom on the chlorine atom stabilizes the conjugate base.
 (C) $\text{HClO}_2(aq)$ is the stronger acid because its molecules experience weaker London dispersion forces.
 (D) $\text{HClO}_2(aq)$ is the stronger acid because the lone pairs of electrons on the chlorine atom stabilize the conjugate base.

39. If equal masses of the following compounds undergo complete combustion, which will yield the greatest mass of CO_2 ?

- (A) Benzene, C_6H_6
 (B) Cyclohexane, C_6H_{12}
 (C) Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$
 (D) Methane, CH_4



$$\Delta H^\circ = 178 \text{ kJ/mol}_{\text{rxn}}$$

40. The reaction system represented above is at equilibrium. Which of the following will decrease the amount of $\text{CaO}(s)$ in the system?

- (A) Increasing the volume of the reaction vessel at constant temperature
 (B) Lowering the temperature of the system
 (C) Removing some $\text{CO}_2(g)$ at constant temperature
 (D) Removing some $\text{CaCO}_3(s)$ at constant temperature

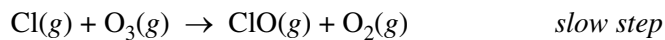
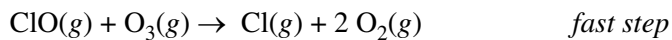
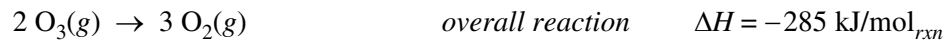
Acid Solution	Volume of NaOH Added (mL)
A	40
B	75
C	115
D	200

41. To maximize the yield in a certain manufacturing process, a solution of a weak monoprotic acid that has a concentration between 0.20 M and 0.30 M is required. Four 100. mL samples of the acid at different concentrations are each titrated with a 0.20 M NaOH solution. The volume of NaOH needed to reach the end point for each sample is given in the table above. Which solution is the most suitable to maximize the yield?

- (A) Solution A
 (B) Solution B
 (C) Solution C
 (D) Solution D

Questions 42-44 refer to the following information.

When free $\text{Cl}(g)$ atoms encounter $\text{O}_3(g)$ molecules in the upper atmosphere, the following reaction mechanism is proposed to occur.



42. Which of the following rate laws for the overall reaction corresponds to the proposed mechanism?

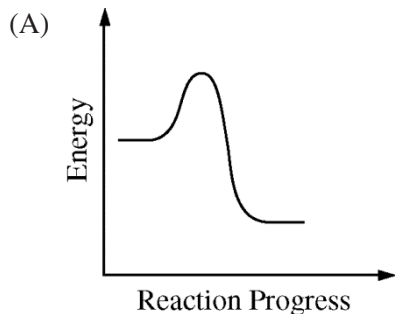
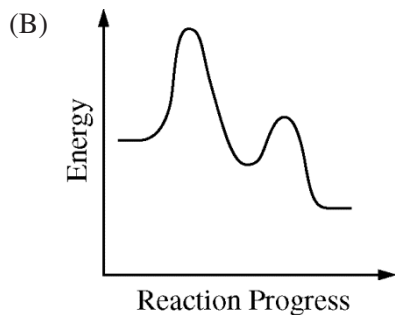
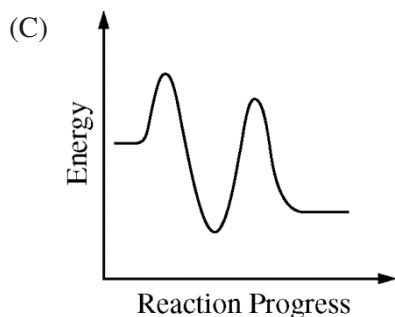
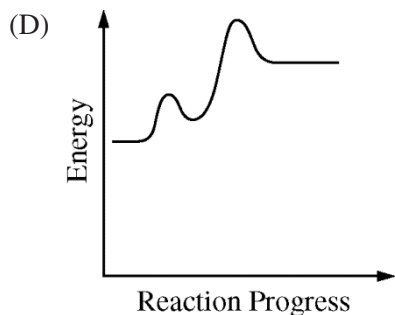
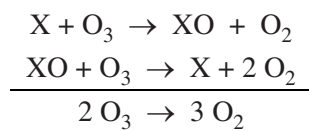
(A) $\text{Rate} = k[\text{O}_3]^2$

(B) $\text{Rate} = k[\text{Cl}][\text{O}_3]$

(C) $\text{Rate} = k[\text{ClO}][\text{O}_3]^2$

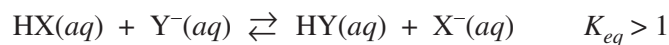
(D) $\text{Rate} = k \frac{[\text{O}_2]^3}{[\text{O}_3]^2}$

43. Which of the following reaction energy profiles best corresponds to the proposed mechanism?



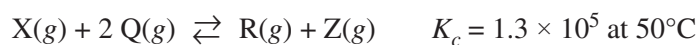
44. The proposed mechanism can be written in a more general form, as shown above. Species other than Cl can also decompose O_3 through the same mechanism. Which of the following chemical species is most likely to decompose O_3 in the upper atmosphere through the above mechanism?

- (A) He
- (B) Br
- (C) N_2
- (D) O_2



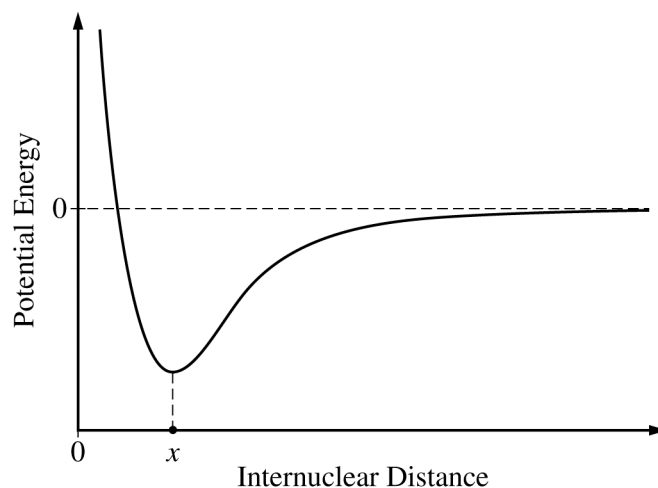
45. A solution of a salt of a weak acid HY is added to a solution of another weak acid HX. Based on the information given above, which of the following species is the strongest base?

(A) $\text{HX}(aq)$
(B) $\text{Y}^-(aq)$
(C) $\text{HY}(aq)$
(D) $\text{X}^-(aq)$

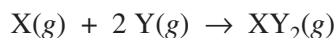


46. A 1.0 mol sample of $\text{X}(g)$ and a 1.0 mol sample of $\text{Q}(g)$ are introduced into an evacuated, rigid 10.0 L container and allowed to reach equilibrium at 50°C according to the equation above. At equilibrium, which of the following is true about the concentrations of the gases?

(A) $[\text{R}] = \frac{1}{2} [\text{Q}]$
(B) $[\text{Q}] = \frac{1}{2} [\text{X}]$
(C) $[\text{R}] = [\text{Z}] > [\text{Q}]$
(D) $[\text{X}] = [\text{Q}] = [\text{R}] = [\text{Z}]$



47. The potential energy of a system of two atoms as a function of their internuclear distance is shown in the diagram above. Which of the following is true regarding the forces between the atoms when their internuclear distance is x ?
- (A) The attractive and repulsive forces are balanced, so the atoms will maintain an average internuclear distance x .
 - (B) There is a net repulsive force pushing the atoms apart, so the atoms will move further apart.
 - (C) There is a net attractive force pulling the atoms together, so the atoms will move closer together.
 - (D) It cannot be determined whether the forces between atoms are balanced, attractive, or repulsive, because the diagram shows only the potential energy.

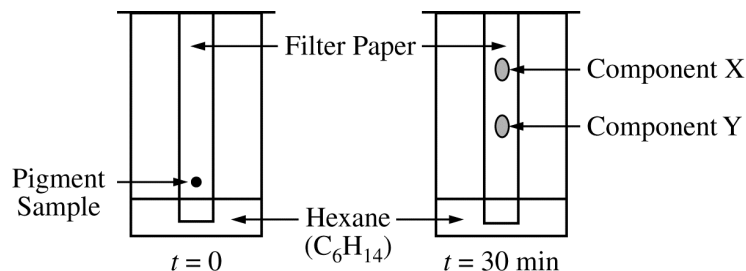


48. In order to determine the order of the reaction represented above, the initial rate of formation of XY_2 is measured using different initial values of $[\text{X}]$ and $[\text{Y}]$. The results of the experiment are shown in the table below.

Trial	$[\text{X}]$	$[\text{Y}]$	Initial Rate of Formation of XY_2 (M s^{-1})
1	0.50	0.50	8.0×10^{-3}
2	1.00	0.50	3.2×10^{-2}
3	1.00	1.00	6.4×10^{-2}

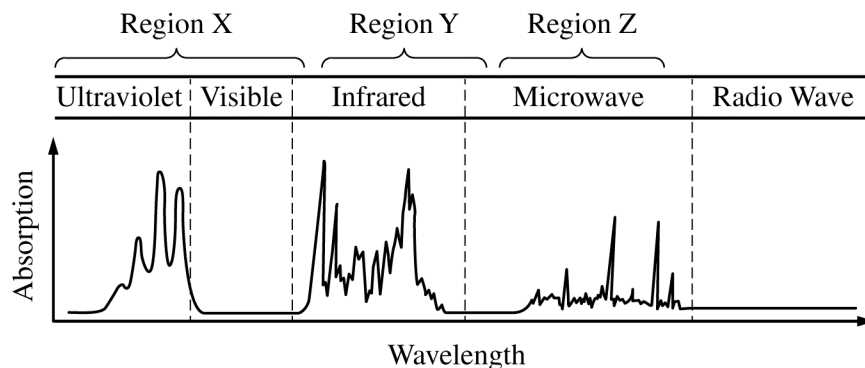
In trial 2 which of the reactants would be consumed more rapidly, and why?

- (A) X, because it has a higher molar concentration.
 (B) X, because the reaction is second order with respect to X.
 (C) Y, because the reaction is second order with respect to Y.
 (D) Y, because the rate of disappearance will be double that of X.



49. In a paper chromatography experiment, a sample of a pigment is separated into two components, X and Y, as shown in the figure above. The surface of the paper is moderately polar. What can be concluded about X and Y based on the experimental results?
- (A) X has a larger molar mass than Y does.
 (B) Y has a larger molar mass than X does.
 (C) X is more polar than Y.
 (D) Y is more polar than X.

ABSORPTION SPECTRUM



50. The diagram above represents the absorption spectrum for a pure molecular substance. Which of the following correctly indicates the type of transition observed for the substance in each of the regions of the absorption spectrum?

	<u>Region X</u>	<u>Region Y</u>	<u>Region Z</u>
(A)	Molecular vibration	Molecular rotation	Electronic transition
(B)	Electronic transition	Molecular rotation	Molecular vibration
(C)	Molecular rotation	Molecular vibration	Electronic transition
(D)	Electronic transition	Molecular vibration	Molecular rotation

CHEMISTRY

Section II

7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

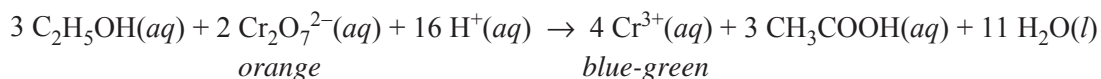
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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.

Half-Reaction	E° (V)
$2 \text{CO}_2(\text{g}) + 12 \text{H}^+(\text{aq}) + 12 e^- \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$	-0.085
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 e^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	1.229

1. A student uses a galvanic cell to determine the concentration of ethanol, $\text{C}_2\text{H}_5\text{OH}$, in an aqueous solution. The cell is based on the half-cell reactions represented in the table above.
 - (a) Write a balanced equation for the overall reaction that occurs in the cell.
 - (b) Calculate E° for the overall reaction that occurs in the cell.
 - (c) A 10.0 mL sample of $\text{C}_2\text{H}_5\text{OH}(\text{aq})$ is put into the electrochemical cell. The cell produces an average current of 0.10 amp for 20. seconds, at which point the $\text{C}_2\text{H}_5\text{OH}(\text{aq})$ has been totally consumed.
 - (i) Calculate the charge, in coulombs, that passed through the cell.
 - (ii) Calculate the initial $[\text{C}_2\text{H}_5\text{OH}]$ in the solution.

An alternative approach to determine the concentration of $\text{C}_2\text{H}_5\text{OH}(\text{aq})$ in a solution is based on the reaction represented below.



A solution has an initial $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ concentration of $1.0 \times 10^{-3} \text{ M}$ and an initial $\text{C}_2\text{H}_5\text{OH}(\text{aq})$ concentration of 0.500 M . The solution contains enough strong acid to keep the pH essentially constant throughout the reaction. The student places a sample of the solution in a cuvette that has a path length of 0.50 cm and places it in a spectrophotometer set to measure absorbance at 440 nm . ($\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ is the only species in the reaction mixture that absorbs light at this wavelength.) The absorbance of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ in the solution is monitored as the reaction proceeds; the table below shows the absorbance as a function of time for the first trial.

Time (min)	Absorbance at 440 nm
0.00	0.782
1.50	0.553
3.00	0.389
4.50	0.278
6.00	0.194

- (d) Calculate the value of $[\text{Cr}_2\text{O}_7^{2-}]$ at 1.50 min .
- (e) The student runs a second trial but this time uses a cuvette that has a path length of 1.00 cm . Describe how the experimental setup should be adjusted to keep the initial absorbance at 0.782 . Justify your answer with respect to the factors that influence the absorbance of a sample in a spectrophotometer.

For the concentrations of reactants used in the experiment, the rate of the reaction can be written as follows.

$$\text{Rate} = k_{\text{observed}}[\text{Cr}_2\text{O}_7^{2-}]^y, \text{ where } k_{\text{observed}} = k[\text{C}_2\text{H}_5\text{OH}]$$

- (f) Explain how the experimental data indicate that the reaction is first order with respect to $\text{Cr}_2\text{O}_7^{2-}$.

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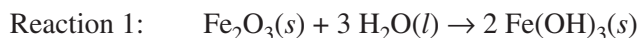
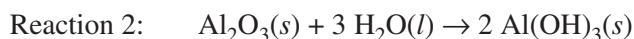
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2. Answer the following questions about Fe and Al compounds.

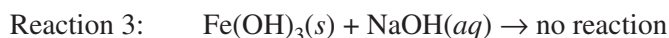
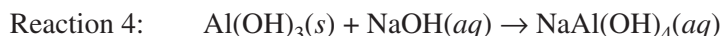
- (a) $\text{Fe}_2\text{O}_3(s)$ and $\text{Al}_2\text{O}_3(s)$ have similar chemical properties; some similarities are due to the oxides having similar lattice energies. Give two reasons why the lattice energies of the oxides are similar.

Use the following reactions that involve Fe and Al compounds to answer parts (b) and (c).

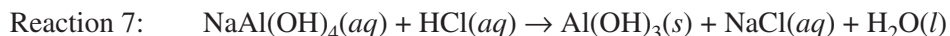
In distilled water



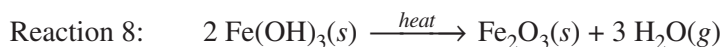
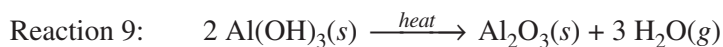
In base



In acid



When heated



Compound	K_{sp}
$\text{Fe}(\text{OH})_3$	4×10^{-38}
$\text{Al}(\text{OH})_3$	1×10^{-33}

- (b) The K_{sp} values for $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ are given in the table above. A 1.0 g sample of powdered $\text{Fe}_2\text{O}_3(s)$ and a 1.0 g sample of powdered $\text{Al}_2\text{O}_3(s)$ are mixed together and placed in 1.0 L of distilled water.
- Which ion, $\text{Fe}^{3+}(aq)$ or $\text{Al}^{3+}(aq)$, will be present in the higher concentration? Justify your answer with respect to the K_{sp} values provided.
 - Write a balanced chemical equation for the dissolution reaction that results in the production of the ion that you identified in part (i).
- (c) Students are asked to develop a plan for separating $\text{Al}_2\text{O}_3(s)$ from a mixture of powdered $\text{Fe}_2\text{O}_3(s)$ and powdered $\text{Al}_2\text{O}_3(s)$ using chemical reactions and laboratory techniques.
- One student proposes that $\text{Al}_2\text{O}_3(s)$ can be separated from the mixture by adding water to the mixture and then filtering. Explain why this approach is not reasonable.

- (ii) A second student organizes a plan using a table. The first two steps have already been entered in the table, as shown below. Complete the plan by listing the additional steps that are needed to recover the $\text{Al}_2\text{O}_3(\text{s})$. List the steps in the correct order and refer to the appropriate reaction by number, if applicable.

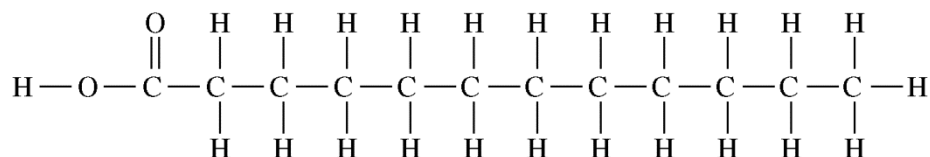
Step	Description	Reaction(s)
1	Add $\text{NaOH}(aq)$ to convert $\text{Al}_2\text{O}_3(s)$ to $\text{Al}(\text{OH})_3(s)$ and then to $\text{NaAl}(\text{OH})_4(aq)$.	2 and 4
2	Filter out the solid $\text{Fe}(\text{OH})_3$ from the mixture and save the filtrate.	—
3		
4		
5		

- (iii) The second student recovers 5.5 g of $\text{Al}_2\text{O}_3(\text{s})$ from a 10.0 g sample of the mixture. Calculate the percent of Al by mass in the mixture of the two powdered oxides. (The molar mass of Al_2O_3 is 101.96 g/mol, and the molar mass of Fe_2O_3 is 159.70 g/mol.)

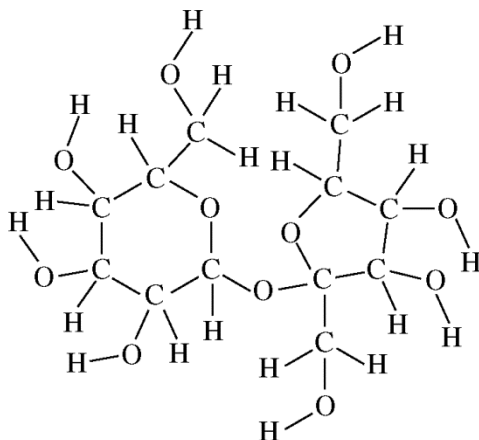
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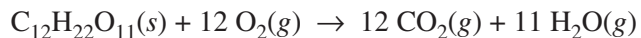
Lauric Acid



Sucrose

3. The structures of two compounds commonly found in food, lauric acid, $\text{C}_{12}\text{H}_{24}\text{O}_2$, and sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, are shown above.
- Which compound, lauric acid or sucrose, is more soluble in water? Justify your answer in terms of the intermolecular forces present between water and each of the compounds.
 - Assume that a 1.5 g sample of lauric acid is combusted and all of the heat energy released is transferred to a 325 g sample of water initially at 25°C . Calculate the final temperature of the water if $\Delta H_{\text{combustion}}$ of lauric acid is -37 kJ/g and the specific heat of water is $4.18 \text{ J/(g}\cdot\text{K)}$.
 - In an attempt to determine $\Delta H_{\text{combustion}}$ of lauric acid experimentally, a student places a 1.5 g sample of lauric acid in a ceramic dish underneath a can made of Al containing 325 g of water at 25°C . The student ignites the sample of lauric acid with a match and records the highest temperature reached by the water in the can.
 - The experiment is repeated using a can of the same mass, but this time the can is made of Cu. The specific heat of Cu is $0.39 \text{ J/(g}\cdot\text{K)}$, and the specific heat of Al is $0.90 \text{ J/(g}\cdot\text{K)}$. Will the final temperature of the water in the can made of Cu be greater than, less than, or equal to the final temperature of the water in the can made of Al? Justify your answer.
 - In both experiments it was observed that the measured final temperature of the water was less than the final temperature calculated in part (b). Identify one source of experimental error that might account for this discrepancy and explain why the error would make the measured final temperature of the water lower than predicted.

- (d) The experiment described above is repeated using a 1.5 g sample of sucrose. The combustion reaction for sucrose in air is represented below.



- Even though ΔG° for the combustion of sucrose in air has a value of $-5837 \text{ kJ/mol}_{rxn}$, the combustion reaction does not take place unless it is ignited. Explain.
- Predict the sign of ΔS° for the reaction and justify your prediction.

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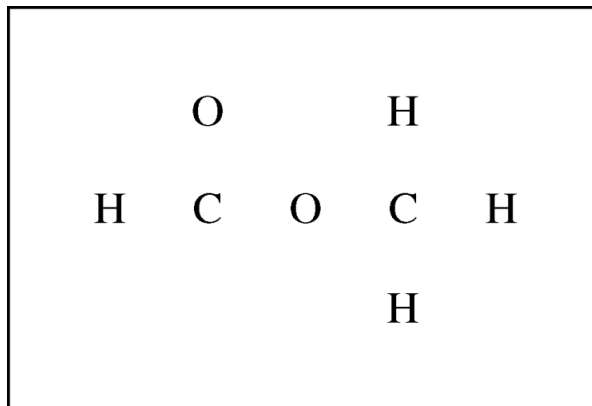
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5. Answer the following questions about two isomers, methyl methanoate and ethanoic acid. The molecular formula of the compounds is $C_2H_4O_2$.

(a) Complete the Lewis electron-dot diagram of methyl methanoate in the box below. Show all valence electrons.



A student puts 0.020 mol of methyl methanoate into a previously evacuated rigid 1.0 L vessel at 450 K. The pressure is measured to be 0.74 atm. When the experiment is repeated using 0.020 mol of ethanoic acid instead of methyl methanoate, the measured pressure is lower than 0.74 atm. The lower pressure for ethanoic acid is due to the following reversible reaction.



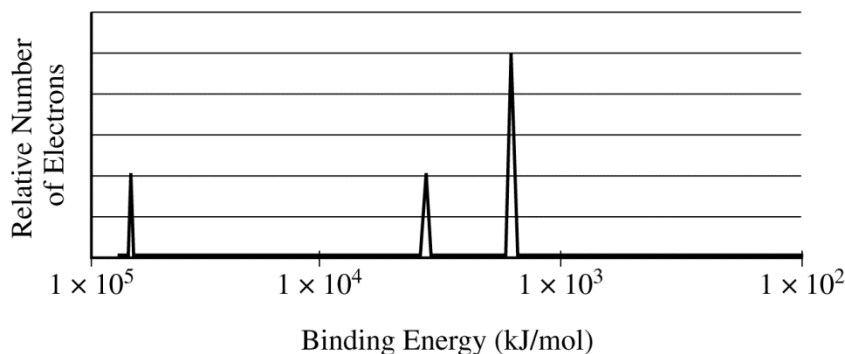
(b) Assume that when equilibrium has been reached, 50. percent of the ethanoic acid molecules have reacted.

(i) Calculate the total pressure in the vessel at equilibrium at 450 K.

(ii) Calculate the value of the equilibrium constant, K_p , for the reaction at 450 K.

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PHOTOELECTRON SPECTRUM



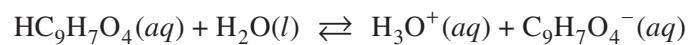
Peak 1	Peak 2	Peak 3
6.72×10^4 kJ/mol	3.88×10^3 kJ/mol	1.68×10^3 kJ/mol

6. The complete photoelectron spectrum of an unknown element is shown above. The frequency ranges of different regions of the electromagnetic spectrum are given in the table below.

Region of Electromagnetic Spectrum	Frequency Range (s^{-1})
Infrared (IR)	1×10^{12} to 4×10^{14}
Ultraviolet/visible (UV/vis)	4×10^{14} to 5×10^{16}
X-rays	5×10^{16} to 1×10^{19}
Gamma rays	$> 1 \times 10^{19}$

- (a) To generate the spectrum above, a source capable of producing electromagnetic radiation with an energy of 7×10^4 kJ per mole of photons was used. Such radiation is from which region of the electromagnetic spectrum? Justify your answer with a calculation.
- (b) A student examines the spectrum and proposes that the second ionization energy of the element is 3.88×10^3 kJ/mol. To refute the proposed interpretation of the spectrum, identify the following.
- The subshell from which an electron is removed in the second ionization of an atom of the element
 - The subshell that corresponds to the second peak of the photoelectron spectrum above

[illegible]



7. The molecular formula of acetylsalicylic acid, also known as aspirin, is $\text{HC}_9\text{H}_7\text{O}_4$. The dissociation of $\text{HC}_9\text{H}_7\text{O}_4(aq)$ is represented by the equation above. The pH of $0.0100\text{ M HC}_9\text{H}_7\text{O}_4(aq)$ is measured to be 2.78.
- (a) Write the expression for the equilibrium constant, K_a , for the reaction above.
- (b) Calculate the value of K_a for acetylsalicylic acid.
- (c) An aqueous solution of aspirin is buffered to have equal concentrations of $\text{HC}_9\text{H}_7\text{O}_4(aq)$ and $\text{C}_9\text{H}_7\text{O}_4^-(aq)$. Calculate the pH of the solution.

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This image shows a single sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

1	PERIODIC TABLE OF THE ELEMENTS																18
1	2															2	He
1.008																4.00	
3	4	5	6	7	8	9											10
Li	Be	B	C	N	O	F											Ne
6.94	9.01	10.81	12.01	14.01	16.00	19.00											20.18
11	12	13	14	15	16	17											18
Na	Mg	Al	Si	P	S	Cl											Ar
22.99	24.30	26.98	28.09	30.97	32.06	35.45											39.95
19	20	21	22	23	24	25	26	27	28	29	30						36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						Kr
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38						83.80
37	38	39	40	41	42	43	44	45	46	47	48						54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						Xe
85.47	87.62	88.91	91.22	92.91	95.95	(97)	101.1	102.91	106.42	107.87	112.41						131.29
55	56	57	72	73	74	75	76	77	78	79	80						86
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						Rn
132.91	137.33	138.91	178.49	180.95	183.84	186.21	190.2	192.2	195.08	196.97	200.59						(222)
87	88	89	104	105	106	107	108	109	110	111	112						118
Fr	Ra	†Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						Uuo
(223)	(226)	(227)	(267)	(270)	(271)	(270)	(277)	(276)	(281)	(282)	(285)						(294)

*Lanthanoid Series

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

†Actinoid Series

AP[®] CHEMISTRY EQUATIONS AND CONSTANTS

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

L, mL = liter(s), milliliter(s)
g = gram(s)
nm = nanometer(s)
atm = atmosphere(s)

mm Hg = millimeters of mercury
J, kJ = joule(s), kilojoule(s)
V = volt(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

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

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

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

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

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

$$= K_a \times K_b$$

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

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

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

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

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

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

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

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

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, R = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

$$\text{STP} = 273.15 \text{ K and } 1.0 \text{ atm}$$

$$\text{Ideal gas at STP} = 22.4 \text{ L mol}^{-1}$$

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

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

$$= -RT \ln K$$

$$= -nFE^\circ$$

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

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

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

APPENDIX - ANSWERS

AP CHEMISTRY 2015

Multiple-choice key transcribed from the matching supplied source.

Question	Answer	Question	Answer	Question	Answer
1	A	18	B	35	C
2	C	19	B	36	A
3	D	20	B	37	B
4	A	21	D	38	B
5	C	22	B	39	A
6	C	23	C	40	B
7	C	24	B	41	C
8	B	25	C	42	B
9	A	26	A	43	B
10	D	27	B	44	B
11	B	28	B	45	B
12	B	29	B	46	C
13	A	30	B	47	A
14	A	31	D	48	D
15	D	32	B	49	D
16	B	33	D	50	D
17	C	34	D		

This supplied modified practice paper contains 50 MCQs and 7 FRQs.

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Question 1

Half-Reaction	E° (V)
$2 \text{CO}_2(g) + 12 \text{H}^+(aq) + 12 e^- \rightarrow \text{C}_2\text{H}_5\text{OH}(aq) + 3 \text{H}_2\text{O}(l)$	-0.085
$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.229

A student uses a galvanic cell to determine the concentration of ethanol, $\text{C}_2\text{H}_5\text{OH}(aq)$, in an aqueous solution. The cell is based on the half-cell reactions represented in the table above.

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

$\text{C}_2\text{H}_5\text{OH}(aq) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(l)$	<p>1 point is earned for the correct reactants and products.</p> <p>1 point is earned for balancing the equation.</p>
--	---

(b) Calculate E° for the overall reaction that occurs in the cell.

$E^\circ = -(-0.085 \text{ V}) + 1.229 \text{ V} = +1.314 \text{ V}$	1 point is earned for a correct answer that is consistent with the equation in part (a).
--	--

(c) A 10.0 mL sample of $\text{C}_2\text{H}_5\text{OH}(aq)$ is put into the electrochemical cell. The cell produces an average current of 0.10 amp for 20. seconds, at which point the $\text{C}_2\text{H}_5\text{OH}(aq)$ has been totally consumed.

(i) Calculate the charge, in coulombs, that passed through the cell.

$I = \frac{q}{t} \Rightarrow q = It = 0.10 \text{ amp} \times 20. \text{ s} = 2.0 \text{ C}$	1 point is earned for the correct charge.
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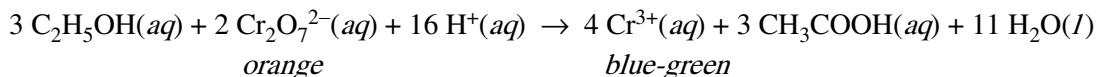
(ii) Calculate the initial $[\text{C}_2\text{H}_5\text{OH}]$ in the solution.

$2.0 \text{ C} \times \frac{1 \text{ mol } e^-}{96,485 \text{ C}} \times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{12 \text{ mol } e^-} = 1.7 \times 10^{-6} \text{ mol } \text{C}_2\text{H}_5\text{OH}$ $\frac{1.7 \times 10^{-6} \text{ mol } \text{C}_2\text{H}_5\text{OH}}{10.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1.0 \text{ L}} = 1.7 \times 10^{-4} \text{ M}$	<p>1 point is earned for the number of moles of $\text{C}_2\text{H}_5\text{OH}$.</p> <p>1 point is earned for the initial molarity of $\text{C}_2\text{H}_5\text{OH}$.</p>
--	--

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Question 1 (continued)

An alternative approach to determine the concentration of $\text{C}_2\text{H}_5\text{OH}(aq)$ in a solution is based on the reaction represented below.



A solution has an initial $\text{Cr}_2\text{O}_7^{2-}(aq)$ concentration of $1.0 \times 10^{-3} M$ and an initial $\text{C}_2\text{H}_5\text{OH}(aq)$ concentration of $0.500 M$. The solution contains enough strong acid to keep the pH essentially constant throughout the reaction. The student places a sample of the solution in a cuvette that has a path length of 0.50 cm and places it in a spectrophotometer set to measure absorbance at 440 nm . ($\text{Cr}_2\text{O}_7^{2-}(aq)$ is the only species in the reaction mixture that absorbs light at this wavelength.) The absorbance of $\text{Cr}_2\text{O}_7^{2-}(aq)$ in the solution is monitored as the reaction proceeds; the table below shows the absorbance as a function of time for the first trial.

Time (min)	Absorbance at 440 nm
0.00	0.782
1.50	0.553
3.00	0.389
4.50	0.278
6.00	0.194

(d) Calculate the value of $[\text{Cr}_2\text{O}_7^{2-}]$ at 1.50 min .

<p>Absorbance is proportional to $[\text{Cr}_2\text{O}_7^{2-}]$.</p> $\frac{1.0 \times 10^{-3} M}{0.782} = \frac{x}{0.553}$ $x = 7.1 \times 10^{-4} M$ <p>OR</p> <p>Initial condition: $a = \frac{A}{bc} = \frac{0.782}{(0.50 \text{ cm})(1.0 \times 10^{-3} M)} = 1564 M^{-1} \text{ cm}^{-1}$</p> <p>At 1.50 min: $c = \frac{A}{ab} = \frac{0.553}{(1564 M^{-1} \text{ cm}^{-1})(0.50 \text{ cm})} = 7.1 \times 10^{-4} M$</p>	<p>1 point is earned for the correct concentration.</p>
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Question 1 (continued)

- (e) The student runs a second trial but this time uses a cuvette that has a path length of 1.00 cm. Describe how the experimental setup should be adjusted to keep the initial absorbance at 0.782. Justify your answer with respect to the factors that influence the absorbance of a sample in a spectrophotometer.

$A = abc$ If path length (b) is doubled, and molar absorptivity (a) is constant, the initial concentration of $\text{Cr}_2\text{O}_7^{2-}$ (c) must be halved to keep the initial absorbance (A) constant.	1 point is earned for reference to a factor that affects absorbance. 1 point is earned for the correct adjustment.
---	---

For the concentrations of reactants used in the experiment, the rate of the reaction can be written as follows.

$$\text{Rate} = k_{\text{observed}}[\text{Cr}_2\text{O}_7^{2-}]^y, \text{ where } k_{\text{observed}} = k[\text{C}_2\text{H}_5\text{OH}]$$

- (f) Explain how the experimental data indicate that the reaction is first order with respect to $\text{Cr}_2\text{O}_7^{2-}$.

Absorbance is proportional to concentration of $\text{Cr}_2\text{O}_7^{2-}$. Absorbance is halved after 3.00 min and again after another 3.00 min. Thus the half-life of the reaction is constant, so the reaction must be first order with respect to $\text{Cr}_2\text{O}_7^{2-}$. OR Demonstration that the rate of change in $\ln(A)$ over time is constant.	1 point is earned for a correct explanation that uses the data.
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Question 2

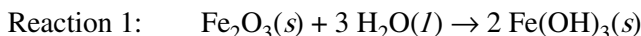
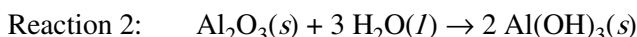
Answer the following questions about Fe and Al compounds.

- (a) $\text{Fe}_2\text{O}_3(s)$ and $\text{Al}_2\text{O}_3(s)$ have similar chemical properties; some similarities are due to the oxides having similar lattice energies. Give two reasons why the lattice energies of the oxides are similar.

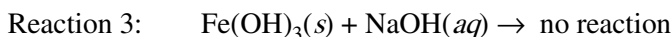
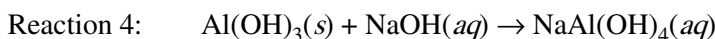
Fe^{3+} and Al^{3+} have similar sizes (radii). Fe^{3+} and Al^{3+} have the same charge.	1 point is earned for <u>each</u> reason.
--	---

Use the following reactions that involve Fe and Al compounds to answer parts (b) and (c).

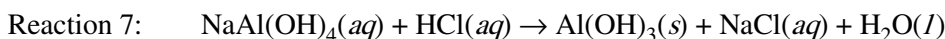
In distilled water



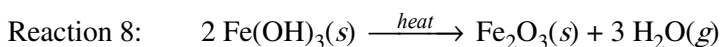
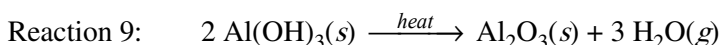
In base



In acid



When heated



Compound	K_{sp}
$\text{Fe}(\text{OH})_3$	4×10^{-38}
$\text{Al}(\text{OH})_3$	1×10^{-33}

- (b) The K_{sp} values for $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ are given in the table above. A 1.0 g sample of powdered $\text{Fe}_2\text{O}_3(s)$ and a 1.0 g sample of powdered $\text{Al}_2\text{O}_3(s)$ are mixed together and placed in 1.0 L of distilled water.

- (i) Which ion, $\text{Fe}^{3+}(aq)$ or $\text{Al}^{3+}(aq)$, will be present in the higher concentration? Justify your answer with respect to the K_{sp} values provided.

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Question 2 (continued)

Al^{3+} will be present in higher concentration. $\text{Al}(\text{OH})_3$ has the same stoichiometry as $\text{Fe}(\text{OH})_3$ but a greater K_{sp} .	1 point is earned for the correct choice and explanation.
---	---

- (ii) Write a balanced chemical equation for the dissolution reaction that results in the production of the ion that you identified in part (i).

$\text{Al}(\text{OH})_3(s) \rightarrow \text{Al}^{3+}(aq) + 3 \text{OH}^{-}(aq)$ OR $\text{Al}_2\text{O}_3(s) + 3 \text{H}_2\text{O}(l) \rightarrow 2 \text{Al}^{3+}(aq) + 6 \text{OH}^{-}(aq)$	1 point is earned for a balanced equation.
---	--

- (c) Students are asked to develop a plan for separating $\text{Al}_2\text{O}_3(s)$ from a mixture of powdered $\text{Fe}_2\text{O}_3(s)$ and powdered $\text{Al}_2\text{O}_3(s)$ using chemical reactions and laboratory techniques.

- (i) One student proposes that $\text{Al}_2\text{O}_3(s)$ can be separated from the mixture by adding water to the mixture and then filtering. Explain why this approach is not reasonable.

This approach only works when there is a significant difference in water solubility between two substances.	1 point is earned for a correct explanation.
---	--

- (ii) A second student organizes a plan using a table. The first two steps have already been entered in the table, as shown below. Complete the plan by listing the additional steps that are needed to recover the $\text{Al}_2\text{O}_3(s)$. List the steps in the correct order and refer to the appropriate reaction by number, if applicable.

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Question 2 (continued)

Step	Description	Reaction(s)
1	Add $\text{NaOH}(aq)$ to convert $\text{Al}_2\text{O}_3(s)$ to $\text{Al}(\text{OH})_3(s)$ and then to $\text{NaAl}(\text{OH})_4(aq)$.	2 and 4
2	Filter out the solid $\text{Fe}(\text{OH})_3$ from the mixture and save the filtrate.	—
3	<i>Add HCl to the filtrate until a precipitate of $\text{Al}(\text{OH})_3$ forms.</i>	7
4	<i>Filter out the solid $\text{Al}(\text{OH})_3$.</i>	—
5	<i>Heat the solid $\text{Al}(\text{OH})_3$ to form Al_2O_3.</i>	9

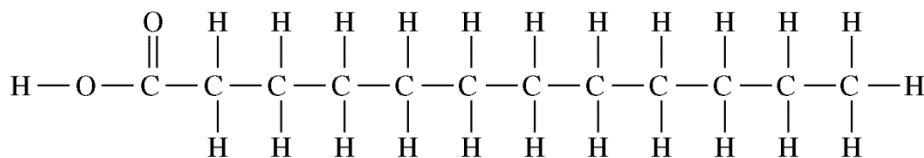
(See rows 3-5 in table.)	1 point is earned for each correct row (description plus reaction number, if applicable).
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- (iii) The second student recovers 5.5 g of $\text{Al}_2\text{O}_3(s)$ from a 10.0 g sample of the mixture.
 Calculate the percent of Al by mass in the mixture of the two powdered oxides.
 (The molar mass of Al_2O_3 is 101.96 g/mol, and the molar mass of Fe_2O_3 is 159.70 g/mol.)

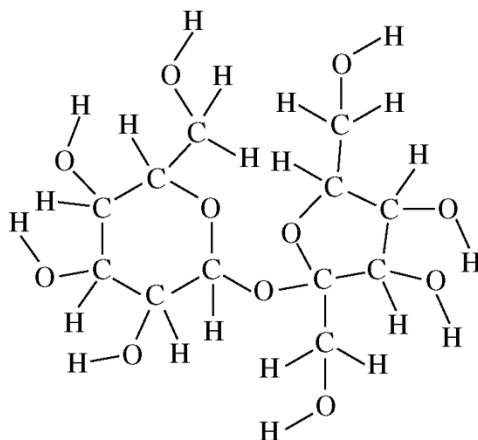
$5.5 \text{ g Al}_2\text{O}_3 \times \frac{1 \text{ mol Al}_2\text{O}_3}{101.96 \text{ g Al}_2\text{O}_3} \times \frac{2 \text{ mol Al}}{1 \text{ mol Al}_2\text{O}_3} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 2.9 \text{ g Al}$ $\frac{2.9 \text{ g}}{10.0 \text{ g}} \times 100 = 29\%$	<p>1 point is earned for the number of grams of Al.</p> <p>1 point is earned for the mass percent Al.</p>
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Question 3



Lauric Acid



Sucrose

The structures of two compounds commonly found in food, lauric acid, $\text{C}_{12}\text{H}_{24}\text{O}_2$, and sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, are shown above.

- (a) Which compound, lauric acid or sucrose, is more soluble in water? Justify your answer in terms of the intermolecular forces present between water and each of the compounds.

Sucrose is more soluble than lauric acid. Stronger interactions occur between sucrose and water molecules due to a greater capacity for hydrogen bonding as a result of a larger number of $-\text{OH}$ groups in sucrose. Although lauric acid molecules have one site for hydrogen bonding, the long hydrocarbon chain causes London dispersion forces to be the predominant, yet weaker, interaction with water molecules.

1 point is earned for discussion of hydrogen bonding between each substance and water.

1 point is earned for a valid conclusion about solubility based on a comparison of these forces.

- (b) Assume that a 1.5 g sample of lauric acid is combusted and all of the heat energy released is transferred to a 325 g sample of water initially at 25°C . Calculate the final temperature of the water if $\Delta H_{\text{combustion}}$ of lauric acid is -37 kJ/g and the specific heat of water is $4.18 \text{ J/(g}\cdot\text{K)}$.

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Question 3 (continued)

$37 \text{ kJ/g} \times 1.5 \text{ g} = 56 \text{ kJ released}$ $q = mc\Delta T \Rightarrow \Delta T = \frac{q}{mc} = \frac{56,000 \text{ J}}{(325 \text{ g})(4.18 \text{ J/(g}\cdot\text{K)})} = 41 \text{ K (41}^\circ\text{C)}$ Final temperature = $25^\circ\text{C} + 41^\circ\text{C} = 66^\circ\text{C}$	1 point is earned for heat released. 1 point is earned for a final temperature consistent with the heat released.
---	--

- (c) In an attempt to determine $\Delta H_{\text{combustion}}$ of lauric acid experimentally, a student places a 1.5 g sample of lauric acid in a ceramic dish underneath a can made of Al containing 325 g of water at 25°C . The student ignites the sample of lauric acid with a match and records the highest temperature reached by the water in the can.

- (i) The experiment is repeated using a can of the same mass, but this time the can is made of Cu. The specific heat of Cu is $0.39 \text{ J/(g}\cdot\text{K)}$, and the specific heat of Al is $0.90 \text{ J/(g}\cdot\text{K)}$. Will the final temperature of the water in the can made of Cu be greater than, less than, or equal to the final temperature of the water in the can made of Al? Justify your answer.

The temperature will be greater in the can made of Cu. Since Cu has a lower specific heat than Al, more heat will be absorbed by the water in the Cu can than the water in the Al can.	1 point is earned for the correct answer. 1 point is earned for an appropriate explanation.
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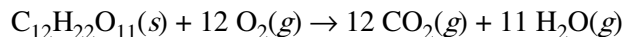
- (ii) In both experiments it was observed that the measured final temperature of the water was less than the final temperature calculated in part (b). Identify one source of experimental error that might account for this discrepancy and explain why the error would make the measured final temperature of the water lower than predicted.

Possible answers include: Heat is lost to the environment. The temperature of the water is lower because less heat is transferred to the water. OR Heat is transferred to the can or thermometer. The temperature of the water is lower because less heat is transferred to the water. OR Incomplete combustion of the lauric acid. The temperature of the water is lower because less heat was released from the combustion reaction.	1 point is earned for a valid source of error. 1 point is earned for an acceptable explanation.
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Question 3 (continued)

- (d) The experiment described above is repeated using a 1.5 g sample of sucrose. The combustion reaction for sucrose in air is represented below.



- (i) Even though ΔG° for the combustion of sucrose in air has a value of $-5837 \text{ kJ/mol}_{rxn}$, the combustion reaction does not take place unless it is ignited. Explain.

The reaction has a high activation energy. The ignition source provides energy to the molecules; some of them can then overcome the activation energy barrier. The reaction is exothermic, so the heat released allows the reaction to continue.	1 point is earned for a correct explanation.
--	--

- (ii) Predict the sign of ΔS° for the reaction and justify your prediction.

ΔS° for the reaction is positive; there are 23 moles of gaseous products for every 12 moles of gaseous reactant.	1 point is earned for the correct sign and justification.
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Question 4

Molecule	Boiling Point of Compound (K)	Dipole Moment (debyes)	Polarizability (10^{-24} cm^3)
HCl	188	1.05	2.63
HBr	207	0.80	3.61
HI	238	0.38	5.44

The boiling points, dipole moments, and polarizabilities of three hydrogen halides are given in the table above.

- (a) Based on the data in the table, what type of intermolecular force among the molecules $\text{HCl}(l)$, $\text{HBr}(l)$, and $\text{HI}(l)$ is able to account for the trend in boiling points? Justify your answer.

London dispersion forces account for the trend in boiling points. As polarizability of the molecules increases, so does the boiling point of the substance. London dispersion forces depend upon the polarizability of molecules, thus more polarizable molecules have stronger intermolecular forces.	1 point is earned for identifying London dispersion forces. 1 point is earned for explaining the link between polarizability and boiling point.
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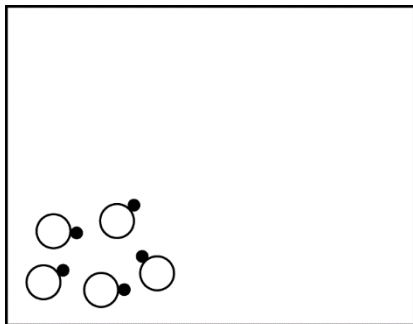
- (b) Based on the data in the table, a student predicts that the boiling point of HF should be 174 K. The observed boiling point of HF is 293 K. Explain the failure of the student's prediction in terms of the types and strengths of the intermolecular forces that exist among HF molecules.

HF molecules have London dispersion forces and hydrogen bonding. The hydrogen bonding is stronger than both regular dipole-dipole forces and London dispersion forces and accounts for HF 's higher boiling point.	1 point is earned for a correct explanation.
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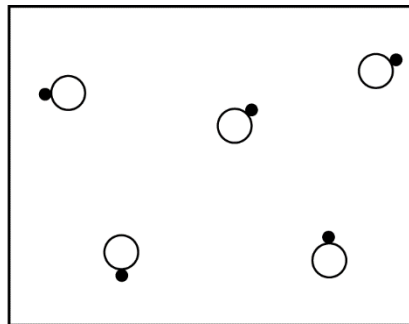
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Question 4 (continued)

- (c) A representation of five molecules of HBr in the liquid state is shown in box 1 below. In box 2, draw a representation of the five molecules of HBr after complete vaporization has occurred.



Box 1



Box 2

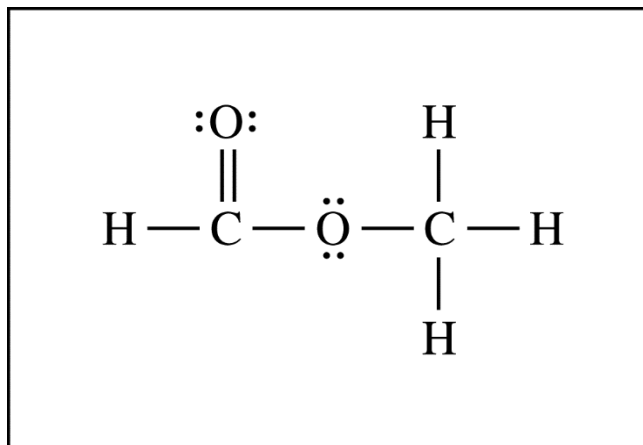
The drawing in Box 2 should show the undissociated molecules randomly distributed throughout the box.	1 point is earned for an acceptable diagram.
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Question 5

Answer the following questions about two isomers, methyl methanoate and ethanoic acid. The molecular formula of the compounds is $\text{C}_2\text{H}_4\text{O}_2$.

- (a) Complete the Lewis electron-dot diagram of methyl methanoate in the box below. Show all valence electrons.



See diagram above.
(Note: A pair of electrons can be drawn as a pair of dots or a line segment.)

1 point is earned for
a correct diagram.

A student puts 0.020 mol of methyl methanoate into a previously evacuated rigid 1.0 L vessel at 450 K. The pressure is measured to be 0.74 atm. When the experiment is repeated using 0.020 mol of ethanoic acid instead of methyl methanoate, the measured pressure is lower than 0.74 atm. The lower pressure for ethanoic acid is due to the following reversible reaction.



- (b) Assume that when equilibrium has been reached, 50. percent of the ethanoic acid molecules have reacted.

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Question 5 (continued)

- (i) Calculate the total pressure in the vessel at equilibrium at 450 K.

<p>Let n_{initial} be the number of moles of gas particles before any reaction occurs. Because 50. percent of the molecules reacted, $n_{\text{final}} = 0.75 n_{\text{initial}}$.</p> $\frac{P_{\text{initial}}}{n_{\text{initial}}} = \frac{P_{\text{final}}}{n_{\text{final}}}$ $n_{\text{CH}_3\text{COOH}} = \frac{0.020 \text{ mol}}{2} = 0.010 \text{ mol}$ $n_{(\text{CH}_3\text{COOH})_2} = \frac{0.010 \text{ mol}}{2} = 0.0050 \text{ mol}$ $P_{\text{final}} = \frac{(P_{\text{initial}})(n_{\text{final}})}{n_{\text{initial}}} = \frac{(0.74 \text{ atm})(0.015 \text{ mol gas particles})}{0.020 \text{ mol gas particles}} = 0.56 \text{ atm}$ <p>OR</p> $PV = nRT$ $P = \frac{(0.015 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(450 \text{ K})}{1.0 \text{ L}} = 0.55 \text{ atm}$	<p>1 point is earned for the correct pressure.</p>
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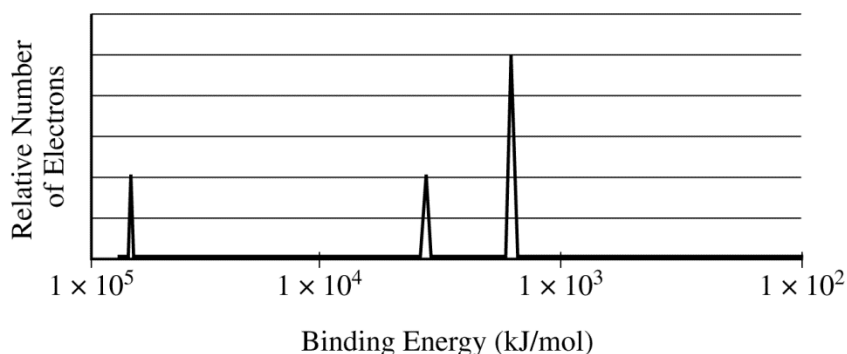
- (ii) Calculate the value of the equilibrium constant, K_p , for the reaction at 450 K.

<p>$P = 0.56 \text{ atm}$</p> <p>Mole fraction $\text{CH}_3\text{COOH} = \frac{0.010 \text{ mol}}{0.015 \text{ mol}} = \frac{2}{3}$</p> <p>Mole fraction $(\text{CH}_3\text{COOH})_2 = \frac{0.0050 \text{ mol}}{0.015 \text{ mol}} = \frac{1}{3}$</p> <p>$P_{\text{CH}_3\text{COOH}} = \frac{2}{3}(0.56 \text{ atm}) = 0.37 \text{ atm}$</p> <p>$P_{(\text{CH}_3\text{COOH})_2} = \frac{1}{3}(0.56 \text{ atm}) = 0.19 \text{ atm}$</p> <p>$K_p = \frac{(P_{(\text{CH}_3\text{COOH})_2})}{(P_{(\text{CH}_3\text{COOH})})^2} = \frac{0.19}{(0.37)^2} = 1.4$</p>	<p>1 point is earned for the correct partial pressures.</p> <p>1 point is earned for an answer that uses partial pressures correctly.</p>
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Question 6

PHOTOELECTRON SPECTRUM



Peak 1	Peak 2	Peak 3
6.72×10^4 kJ/mol	3.88×10^3 kJ/mol	1.68×10^3 kJ/mol

The complete photoelectron spectrum of an unknown element is shown above. The frequency ranges of different regions of the electromagnetic spectrum are given in the table below.

Region of Electromagnetic Spectrum	Frequency Range (s^{-1})
Infrared (IR)	1×10^{12} to 4×10^{14}
Ultraviolet/visible (UV/vis)	4×10^{14} to 5×10^{16}
X-rays	5×10^{16} to 1×10^{19}
Gamma rays	$> 1 \times 10^{19}$

- (a) To generate the spectrum above, a source capable of producing electromagnetic radiation with an energy of 7×10^4 kJ per mole of photons was used. Such radiation is from which region of the electromagnetic spectrum? Justify your answer with a calculation.

$\frac{7 \times 10^4 \text{ kJ}}{1 \text{ mol photons}} \times \frac{1 \text{ mol photons}}{6.022 \times 10^{23} \text{ photons}} = 1.16 \times 10^{-19} \frac{\text{kJ}}{\text{photon}}$ $= 1 \times 10^{-19} \frac{\text{kJ}}{\text{photon}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1 \times 10^{-16} \frac{\text{J}}{\text{photon}}$ $\nu = \frac{E}{h} = \frac{1.16 \times 10^{-16} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.75 \times 10^{17} \text{ s}^{-1} = 2 \times 10^{17} \text{ s}^{-1}$ <p>The radiation is in the X-ray region.</p>	<p>1 point is earned for calculating the amount of energy per photon.</p> <p>1 point is earned for the frequency and region of the spectrum.</p>
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Question 6 (continued)

- (b) A student examines the spectrum and proposes that the second ionization energy of the element is 3.88×10^3 kJ/mol. To refute the proposed interpretation of the spectrum, identify the following.

(i) The subshell from which an electron is removed in the second ionization of an atom of the element

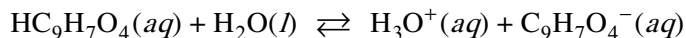
$2p$	1 point is earned for the correct answer.
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(ii) The subshell that corresponds to the second peak of the photoelectron spectrum above

$2s$	1 point is earned for the correct answer.
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Question 7



The molecular formula of acetylsalicylic acid, also known as aspirin, is $\text{HC}_9\text{H}_7\text{O}_4$. The dissociation of $\text{HC}_9\text{H}_7\text{O}_4(aq)$ is represented by the equation above. The pH of $0.0100\text{ M HC}_9\text{H}_7\text{O}_4(aq)$ is measured to be 2.78.

- (a) Write the expression for the equilibrium constant, K_a , for the reaction above.

$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]}$	<p>1 point is earned for the correct expression.</p>
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- (b) Calculate the value of K_a for acetylsalicylic acid.

$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.78} = 1.66 \times 10^{-3}\text{ M}$ $[\text{H}_3\text{O}^+] = [\text{C}_9\text{H}_7\text{O}_4^-] = 1.66 \times 10^{-3}\text{ M}$ $[\text{HC}_9\text{H}_7\text{O}_4] = 0.0100\text{ M} - 1.66 \times 10^{-3}\text{ M}$ $K_a = \frac{(1.66 \times 10^{-3})^2}{0.0100 - (1.66 \times 10^{-3})} = 3.3 \times 10^{-4}$	<p>1 point is earned for the correct $[\text{H}_3\text{O}^+]$.</p> <p>1 point is earned for the value of K_a.</p>
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- (c) An aqueous solution of aspirin is buffered to have equal concentrations of $\text{HC}_9\text{H}_7\text{O}_4(aq)$ and $\text{C}_9\text{H}_7\text{O}_4^-(aq)$. Calculate the pH of the solution.

$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]}$ $= -\log(3.3 \times 10^{-4}) + 0$ $= 3.48$	<p>1 point is earned for a pH consistent with the K_a calculated in part (b).</p>
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