## CHEMISTRY

## SECTION I

**Time—1 hour and 30 minutes**

**60 Questions**

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

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

1. An atom of chlorine and an atom of which of the following elements will form a bond with the most ionic character?

   (A) Germanium
   (B) Carbon
   (C) Copper
   (D) Potassium

$$NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$$

2. The single-step reaction represented above takes place in a sealed container. Which of the following will reduce the value of $k$, the rate constant for the reaction?

   (A) Decreasing the temperature
   (B) Increasing the temperature
   (C) Decreasing the size of the sealed container
   (D) Increasing the size of the sealed container

3. The pH of a solution of 0.009 $M$ KOH$(aq)$ is closest to which of the following?

   (A) 2
   (B) 5
   (C) 9
   (D) 12

4. Which of the following is the ground-state electron configuration for the $Na^+$ ion?

   (A) $1s^2 2s^2 2p^5$
   (B) $1s^2 2s^2 2p^6$
   (C) $1s^2 2s^2 2p^6 3s^1$
   (D) $1s^2 2s^2 2p^6 3s^2$

5. A 1.5 g sample of ice, $H_2O(s)$, at is placed in a warm room. Which of the following best describes the energy transfer involved in melting the ice to create liquid water at 0.0°C? (The heat of fusion of $H_2O(s)$ is 334 J/g.)

   (A) 334 joules of energy is transferred from the ice to the room.
   (B) 334 joules of energy is transferred from the room to the ice.
   (C) 501 joules of energy is transferred from the ice to the room.
   (D) 501 joules of energy is transferred from the room to the ice.

6. A student dissolves a quantity of $KNO_3(s)$ in water. What information must the student use to calculate the molarity of the aqueous solution?

   (A) Grams of $KNO_3$ and the density of water
   (B) Liters of $KNO_3$ and liters of solution
   (C) Moles of $KNO_3$ and the density of water
   (D) Moles of $KNO_3$ and liters of solution

7. A student titrates 25 mL of a 0.10 *M* solution of an unknown acid, HX, with a 0.10 *M* solution of sodium hydroxide, NaOH$(aq)$, to the equivalence point. Which of the following pieces of experimental evidence would best help the student confirm that HX is a weak acid?

   (A) The initial pH of the acid solution is greater than 1.

   (B) The initial pH of the acid solution is less than 1.

   (C) Less than 25 mL of NaOH$(aq)$ is required to reach the equivalence point.

   (D) More than 25 mL of NaOH$(aq)$ is required to reach the equivalence point.

8. Which of the following best explains how the bonding in a metal allows it to be ductile (i.e., allows it to be drawn into a wire)?

   (A) Metal atoms are spherical; therefore, the solid metal can be easily drawn into wires that have a round cross-section.

   (B) Because of strongly directional bonding in the solid metal, the atoms both in front of and behind a given atom in a wire will bind together more strongly than the atoms not along the direction of the wire.

   (C) Because the mobile electrons attract the metal cations equally in all directions, the metal cations can move easily past one another as the metal is drawn into a wire.

   (D) Metal atoms tend to be much smaller than nonmetal atoms; therefore, they can move easily past one another as the metal is drawn into a wire.

9. A 100 g sample of a substance decomposes so that 25 g of the original substance remains after 40 seconds. If the decomposition is first order, which of the following is the rate constant, *k*, of the decomposition reaction?

   (A) 0.017 $s^{-1}$

   (B) 0.035 $s^{-1}$

   (C) 1.4 $s^{-1}$

   (D) 20 $s^{-1}$

10. A student attempts to prepare a buffer solution with a pH of 10.0 by adding $NaHCO_3$ ($pK_a = 10.3$) and $Na_2CO_3$ to distilled water. Instead of the desired pH, the measured pH of the buffer solution is 9.5. Which of the following is the most likely reason that the pH is too low?

    (A) Too much $NaHCO_3$ was used.

    (B) Too much $Na_2CO_3$ was used.

    (C) There was water in the flask before $NaHCO_3$ and $Na_2CO_3$ were added.

    (D) In order to prepare the buffer, a few drops of a strong base should have been added.

11. Which of the following best explains why $H_2(g)$ behaves more ideally than most other gases?

    (A) The number of particles in a given volume of $H_2(g)$ is smallest in comparison to other gases, because the molar mass of $H_2$ is smallest.

    (B) Collisions between gas particles and the walls of a container are more frequent for smaller molecules, because the average velocity is very high.

    (C) The average kinetic energy of $H_2$ molecules at a given temperature is large, because the average velocity of the $H_2$ molecules is very high.

    (D) Intermolecular attractions between $H_2$ molecules are weak, because the electron clouds of $H_2$ molecules are small.

12. Which of the following best accounts for the decrease in the first-ionization energy of the alkaline earth metals going down the group?

    (A) The number of protons in the nucleus increases, resulting in increased attraction between the nucleus and the electron being removed.

    (B) The number of protons in the nucleus increases, resulting in a greater effective nuclear charge attracting the electron being removed.

    (C) The number of electron shells increases, resulting in a greater average distance between the nucleus and the electron being removed.

    (D) The number of electron shells increases, resulting in less shielding between the nucleus and the electron being removed.

| Substance | Specific Heat (J/g·°C) |
|---|---|
| Water | 4.18 |
| Ethanol | 2.44 |
| Fe($s$) | 0.449 |

13. Two identical insulated containers hold equal masses of liquid at the same temperature; one contains water and the other contains ethanol. Two identical cubes of Fe($s$) are heated to the same temperature, one cube is placed in each container, and both systems are allowed to reach thermal equilibrium. Based on the information in the table shown, which of the following best predicts what will be observed?

    (A) Both systems will have the same final temperature because the mass and initial temperature of the liquids are the same.

    (B) Both systems will have the same final temperature because the Fe($s$) cubes will transfer the same amount of heat to both liquids.

    (C) The ethanol system will have the higher final temperature because the specific heat of ethanol is lower than that of water.

    (D) The ethanol system will have the lower final temperature because the specific heat of ethanol is lower than that of water.

$$2\text{NO}(g) + 2\text{H}_2(g) \rightarrow 2\text{N}_2(g) + 2\text{H}_2\text{O}(g)$$

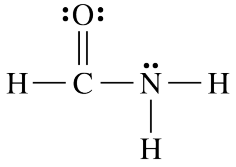
14. The rate law for the reaction shown is rate $= k[\text{NO}]^2[\text{H}_2]$. What is the overall order of the reaction?

    (A) First order

    (B) Second order

    (C) Third order

    (D) Fourth order



15. The complete Lewis electron-dot diagram for $\text{HCONH}_2$ is shown above. Identify the hybridization of the valence orbitals for the carbon atom and the approximate hydrogen-carbon-nitrogen bond angle according to VSEPR theory.

    (A) $sp$ hybridized and 180°

    (B) $sp^2$ hybridized and 120°

    (C) $sp^2$ hybridized and 180°

    (D) $sp^3$hybridized and 120°

$$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \quad K_c = 100$$

16. Equimolar amounts of $\text{H}_2(g)$ and $\text{I}_2(g)$ are pumped into a previously evacuated, rigid 1.0 L container and allowed to attain the equilibrium shown above at a constant temperature. If 0.600 mol of HI($g$) is present at equilibrium, how many moles of $\text{H}_2(g)$ were initially added to the container?

    (A) 0.0036 mol

    (B) 0.060 mol

    (C) 0.36 mol

    (D) 0.60 mol

| | Ionization Energy (kJ/mol) |
|---|---|
| First | 786 |
| Second | 1,577 |
| Third | 3,232 |
| Fourth | 4,356 |
| Fifth | 16,091 |

17. Based on the successive ionization energies of element X shown in the table above, which of the following is most likely the formula of the compound produced when element X reacts with fluorine?

(A) XF

(B) $XF_2$

(C) $XF_4$

(D) $XF_5$

| Lewis Dot Diagram | Boiling Point (°C) |
|---|---|
| H−C≡N: | 26 |
| :N≡N: | −196 |

18. Which of the following best helps to explain why the boiling point of HCN is so much higher than that of $N_2$, as shown by the data in the table above?

(A) HCN contains three atoms, whereas $N_2$ contains two atoms.

(B) HCN is polar, whereas $N_2$ is nonpolar.

(C) HCN has a molar entropy greater than that of $N_2$.

(D) The C≡N bond is stronger than the N≡N bond.

19. A reaction is known to have a negative value of $\Delta H^\circ$ and a positive value of $\Delta S^\circ$. Which of the following statements correctly describes the equilibrium constant, $K_{eq}$, for this reaction?

(A) $K_{eq}$ will be less than 1 only at high temperatures.

(B) $K_{eq}$ will be less than 1 at all temperatures.

(C) $K_{eq}$ will be greater than 1 only at low temperatures.

(D) $K_{eq}$ will be greater than 1 at all temperatures.

| | HX($aq$) | HZ($aq$) |
|---|---|---|
| Conductivity | low | high |

20. A student tests the electrical conductivity of 0.10 $M$ solutions of two different monoprotic acids, HX($aq$) and HZ($aq$). Results from the experiment are shown in the table. Which of the following is a question that could be answered based on the data in the table?

(A) Which acid has the larger $K_a$ value?

(B) Which acid has the larger molar mass?

(C) Which acid solution has the larger density?

(D) Which acid solution has the larger standard molar entropy?

21. A compound made up of only carbon and hydrogen is completely combusted in excess $O_2(g)$. Equimolar quantities of $CO_2(g)$ and $H_2O(g)$ are produced. Which of the following could be the molecular formula of the compound?

(A) $CH_4$

(B) $C_2H_2$

(C) $C_2H_4$

(D) $C_2H_6$

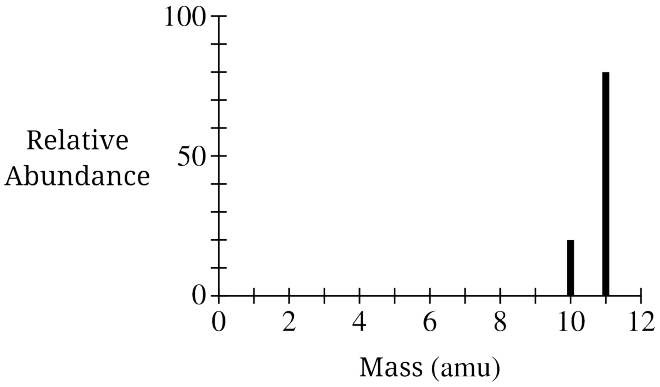
22. Which of the following processes will most likely have a negative $\Delta S^\circ_{rxn}$?

(A) $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$

(B) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

(C) $H_2O(s) \rightarrow H_2O(l)$

(D) $2O_3(g) \rightarrow 3O_2(g)$




23. Based on the mass spectrum of a sample of boron shown above, how many neutrons are in the most common isotope of boron?

(A) 5
(B) 6
(C) 10
(D) 11

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \;\; \Delta H < 0$$

24. Which of the following changes will increase the amount of $NO_2(g)$ in the reaction system at equilibrium represented above?

(A) Adding a catalyst to the reaction system
(B) Increasing the pressure by adding $Ne(g)$ to the system at constant temperature
(C) Increasing the temperature at constant volume
(D) Decreasing the volume at constant temperature

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

25. The rate law for the reaction represented is rate $= k[NO_2]^2[H_2]$. What happens to the rate of the reaction when the concentration of $NO(g)$ is doubled and the concentration of $H_2$(g) is halved?

(A) The rate is halved.
(B) The rate is the same.
(C) The rate is doubled.
(D) The rate is quadrupled.

## Questions 26-28

Students are asked to design an experiment to determine the molarity of a $BaCl_2(aq)$ solution. After examining the $K_{sp}$ values of some barium-containing compounds, the students decide to use 0.100 $M$ $K_2CO_3(aq)$ to precipitate the barium ions. An excess of $K_2CO_3(aq)$ is added to a 50.0 mL sample of the $BaCl_2(aq)$ solution, and the reaction represented by the following equation occurs.

$$BaCl_2(g) + K_2CO_3(aq) \rightarrow BaCO_3(s) + 2KCl(aq)$$

The $BaCO_3(s)$ is filtered, dried, and weighed. The data are recorded in the following table.

| Volume of $Bacl_2(aq)$ | Volume of 0.100 $M$ $K_2CO_3(aq)$ | Mass of $BaCO_3(s)$ |
|---|---|---|
| 50.0 mL | 150.0 mL | 1.97 g |

The molar masses of $BaCl_2$ and $BaCO_3$ are 208 g/mol and 197 g/mol, respectively.

26. Of the following species, which is present in the highest concentration in the filtrate?

    (A) $H^+(aq)$
    (B) $K^+(aq)$
    (C) $Cl^-(aq)$
    (D) $CO_3{}^{2-}(aq)$

27. On the basis of the experimental data, what was $[Ba^{2+}]$ in the original 50.0 mL sample of the solution?

    (A) 0.05 $M$
    (B) 0.10 $M$
    (C) 0.20 $M$
    (D) 0.40 $M$

| Substance | $K_{sp}$ |
|---|---|
| $Ba(NO_3)_2$ | $3.33 \times 10^{-1}$ |
| $BaF_2$ | $1.84 \times 10^{-7}$ |
| $BaSO_4$ | $1.08 \times 10^{-10}$ |
| $BaCrO_4$ | $1.17 \times 10^{-10}$ |

28. Considering the $K_{sp}$ values listed above, which of the following solutions, when used instead of $K_2CO_3(aq)$ in the precipitation procedure, would produce the least number of moles of precipitate?

    (A) 0.200 $M$ $NaNO_3(aq)$
    (B) 0.200 $M$ $NaF(aq)$
    (C) 0.200 $M$ $Na_2SO_4(aq)$
    (D) 0.200 $M$ $Na_2CrO_4(aq)$

## Questions 29-31

Three equimolar gas samples are at the conditions given in the following table. Assume that the gases behave ideally.

| Gas | Volume (L) | Pressure (atm) | Temperature (K) |
|---|---|---|---|
| $F_2$ | 10.0 | 2.0 | 200.0 |
| $N_2$ | 5.0 | 4.0 | 200.0 |
| $O_2$ | 4.0 | 5.0 | 200.0 |

29. Which gas, if any, has the greatest density?

    (A) $F_2$
    (B) $N_2$
    (C) $O_2$
    (D) All three samples have the same density.

30. Which gas, if any, has molecules with the greatest average kinetic energy?

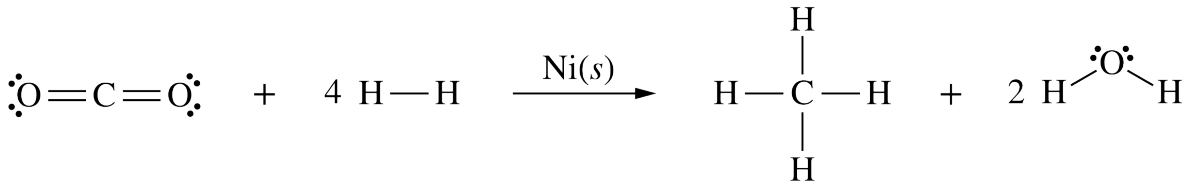
    (A) $F_2$
    (B) $N_2$
    (C) $O_2$
    (D) The molecules in all three samples have the same average kinetic energy.

31. The number of moles of $N_2(g)$ is closest to which of the following?

    (A) 0.10 mol
    (B) 1.2 mol
    (C) 22 mol
    (D) 28 mol

## Questions 32-36

In the gas-phase reaction represented by the following equation, methane ($CH_4$) and water ($H_2O$) are produced from carbon dioxide ($CO_2$) and hydrogen ($H_2$) at high temperature and pressure.




32. Which of the following is a correct statement about oxidation and reduction during the reaction?

    (A) Hydrogen is oxidized, and carbon is reduced.

    (B) Carbon is oxidized, and oxygen is reduced.

    (C) Oxygen is oxidized, and hydrogen is reduced.

    (D) It is not an oxidation-reduction reaction.

33. The reaction is catalyzed by solid nickel. Which of the following describes the effect of the catalyst on the reaction?

    (A) The presence of the catalyst results in an overall reaction that releases less energy.

    (B) The presence of the catalyst results in a reaction pathway that requires a lower activation energy.

    (C) The presence of the catalyst results in an overall reaction that requires more energy.

    (D) The presence of the catalyst results in a reaction pathway that requires a greater activation energy.

34. Based on the Lewis diagrams, which of the products is more soluble in ethanol ($C_2H_5OH$)?

    (A) Methane, because it has more hydrogen atoms than water does, so it can form more hydrogen bonds with ethanol.

    (B) Methane, because it is a larger molecule than water, so its electron cloud is more polarizable.

    (C) Water, because water has a greater molar mass than methane does.

    (D) Water, because water molecules can form hydrogen bonds with ethanol molecules, but methane molecules cannot.

35. Which of the following identifies the hybridization of the valence orbitals of the central atoms of the methane and water molecules?

| | $CH_4$ | $H_2O$ |
|---|---|---|
| (A) | $sp^2$ | $sp$ |
| (B) | $sp^2$ | $sp^2$ |
| (C) | $sp^3$ | $sp^2$ |
| (D) | $sp^3$ | $sp^3$ |

| Substance | Standard Heat of Formation (kJ/mol) |
|---|---|
| $CO_2(g)$ | $-394$ |
| $CH_4(g)$ | $-75$ |
| $H_2(g)$ | 0 |
| $H_2O(g)$ | $-242$ |

36. Based on the information given, $\Delta H_{rxn}$is closest to which of the following?

    (A) $-165$ kJ/mol$_{rxn}$

    (B) $-77$ kJ/mol$_{rxn}$

    (C) $+77$ kJ/mol$_{rxn}$

    (D) $+165$ kJ/mol$_{rxn}$

## Questions 37-40

Gaseous hydrogen and gaseous chlorine can react to form hydrogen chloride gas, as represented by the following equation.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

37. Equimolar amounts of $H_2$ and $Cl_2$ are placed in an evacuated reaction vessel at 500 K. Which of the following statements correctly predicts how the pressure will be affected as the reaction proceeds at a constant temperature and explains why?

    (A) The pressure will remain constant because the number of gas particles is constant.

    (B) The pressure will be halved because one substance is produced from two substances.

    (C) The pressure will increase because the coefficient of HCl in the balanced chemical equation is greater than that of the reactants.

    (D) The pressure will decrease because the average speed of the gaseous product molecules is less than the average speed of the gaseous reactant molecules.

| Bond | Bond Energy (kJ/mol) |
|---|---|
| H−H | 432 |
| Cl−Cl | 239 |
| H−Cl | 427 |

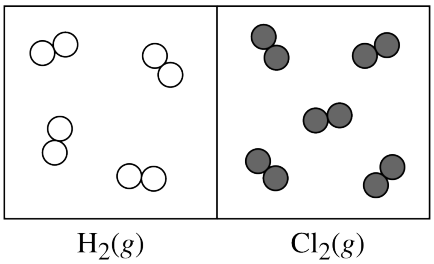
38. Based on the table of bond energies shown, the value of $\Delta H$ for the reaction $H_2 + Cl_2 \rightarrow 2HCl$ is closest to which of the following?

    (A) $-244$ kJ/mol$_{rxn}$

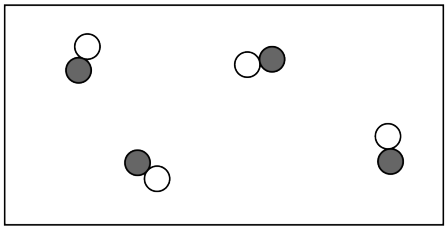
    (B) $-183$ kJ/mol$_{rxn}$

    (C) $+183$ kJ/mol$_{rxn}$

    (D) $+244$ kJ/mol$_{rxn}$




39. The diagrams show particulate representations for samples of gaseous $H_2$ and $Cl_2$ separated by a barrier. After the barrier is removed, the gases react. Which of the following diagrams best represents the mixture if the reaction goes to completion?

(A)


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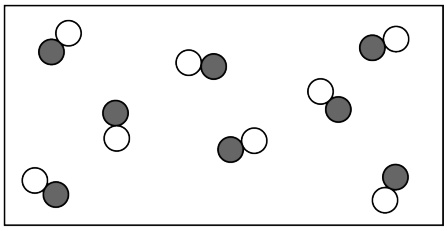

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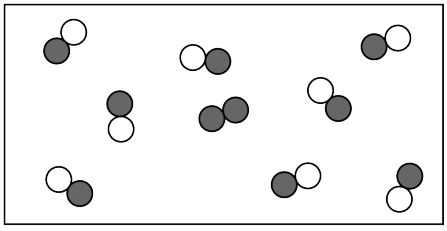
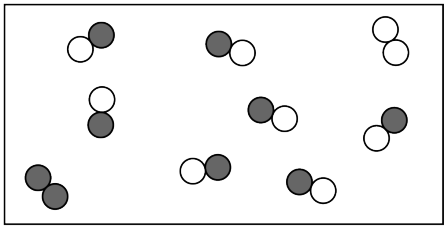


(D)


40. Which of the following correctly ranks the internuclear distances for the $H_2$, $Cl_2$, and HCl molecules from shortest to longest?

(A) $H_2 < Cl_2 < HCl$

(B) $H_2 < HCl < Cl_2$

(C) $Cl_2 < HCl < H_2$

(D) $Cl_2 < H_2 < HCl$

$$Cl_2O(g) + H_2O(g) \rightleftharpoons 2HOCl(g) \quad \Delta H^\circ_{rxn} = +13 \text{ kJ/mol}_{rxn}$$

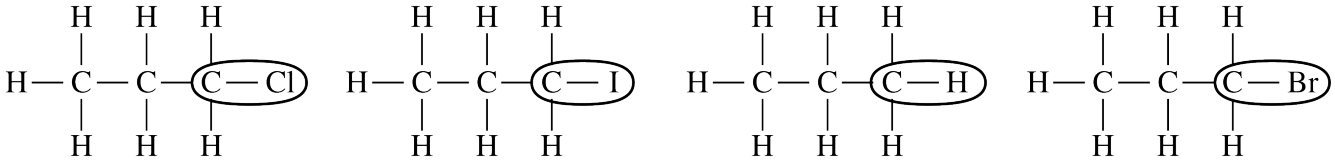
41. A chemical system at equilibrium is represented above. Which of the following changes will increase the number of moles of $HOCl(g)$ present in the system?

(A) Increasing the temperature

(B) Decreasing the volume of the reaction vessel

(C) Adding a catalyst

(D) Removing $Cl_2O(g)$



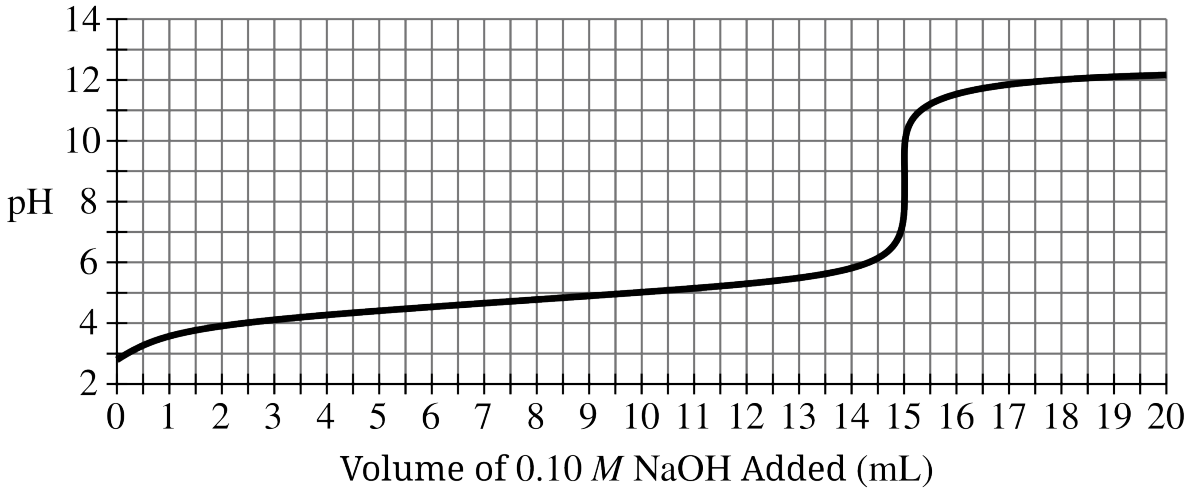

42. Which of the following bonds represented in the diagram above is the most polar?

(A) C−Cl

(B) C−I

(C) C−H

(D) C−Br




43. A sample of an acid is titrated with 0.10 *M* NaOH, and the results are shown in the graph. Based on the pH range of the color change given for each indicator, which of the following indicators would be the best choice for the titration?

(A) Thymol blue; 1.2 – 2.8

(B) Congo red; 3.0 – 5.0

(C) Phenol red; 6.8 – 8.2

(D) Indigo carmine; 11.6 – 14.0

| Half-Reaction | $E^\circ$ (V) |
|---|---|
| $Ag^+(aq) + e^- \rightarrow Ag(s)$ | 0.80 |
| $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ | $-0.25$ |

44. The standard reduction potentials of the half-reactions associated with a galvanic cell are listed in the table above. Which of the following statements identifies the electrode that increases in mass as the cell operates, and correctly explains why?

(A) The Ag electrode, because $Ag^+(aq)$ in the solution is reduced to form $Ag(s)$.

(B) The Ag electrode, because Ag has a greater molar mass than Ni has.

(C) The Ni electrode, because Ni is chemically more reactive than Ag is.

(D) The Ni electrode, because $Ni^{2+}(aq)$ is reduced at a faster rate than $Ag^+(aq)$ is.

$$2H_2S(g) + SO_2(g) \rightleftharpoons 3S(s) + 2H_2O(g) \qquad \Delta H_{rxn} < 0 \text{ and } \Delta G_{rxn} < 0 \text{ at 298 K}$$

45. A 0.20 mol sample of $H_2S(g)$ and a 0.10 mol sample of $SO_2(g)$ are placed in a previously evacuated 10.0 L vessel at 298 K. Even though the reaction represented by the equation above is thermodynamically favorable, the formation of $S(s)$ was not observed. Which of the following best explains why $S(s)$ is not produced at 298 K?

(A) At 298 K, some $S(s)$ must first be present for the reaction to occur.

(B) At 298 K, the value of the equilibrium constant is less than 1.

(C) At 298 K, the energy of most molecular collisions is lower than the activation energy for the reaction.

(D) At 298 K, the loss of entropy is too great to make molecular collisions likely to occur.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \quad K_a = 6.2 \times 10^{-10}$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w = 1.0 \times 10^{-14}$$

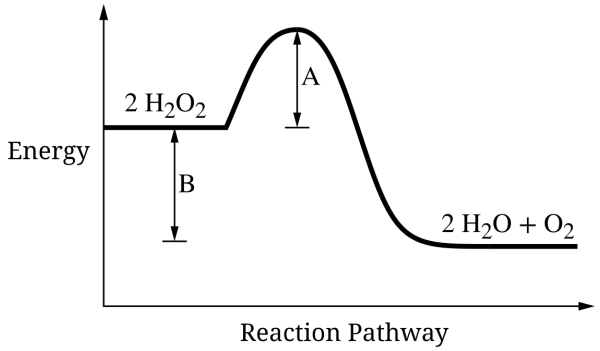
46. Based on the chemical equations given, which of the following statements is correct?

(A) HCN is a weaker acid than $H_2O$.

(B) $CN^-$ is a stronger acid than HCN.

(C) $CN^-$ is a stronger base than $H_2O$.

(D) $H_2O$ is a weaker base than HCN.




47. The potential energy diagram for the uncatalyzed decomposition of $H_2O_2(l)$ is shown above. The arrows labeled A and B represent different amounts of energy. When $I^-(aq)$ is used as a catalyst, how do the magnitudes of A and B in the new reaction energy diagram compare to the uncatalyzed diagram shown above?

| | Energy A | Energy B |
|---|---|---|
| (A) | Larger | Larger |
| (B) | Smaller | Smaller |
| (C) | Smaller | Unchanged |
| (D) | Unchanged | Smaller |

48. Based on the information in the table, which of the following substances produces the most energy per gram of substance combusted?

| Substance | Molar Mass (g/mol) | Heat Released from Combustion of One Mole of Substance (kJ) |
|---|---|---|
| $H_2(l)$ | 2 | 290 |
| $CH_4(l)$ | 16 | 900 |
| $C_2H_5OH(l)$ | 46 | 1,400 |
| $C_{18}H_{38}(l)$ | 254 | 12,000 |

(A) $H_2(l)$
(B) $CH_4(l)$
(C) $C_2H_5OH(l)$
(D) $C_{18}H_{38}(l)$

$$2\text{Cu}(s) + \text{O}_2(g) \rightarrow 2\text{CuO}(s) \quad \Delta H^\circ = -312 \text{ kJ/mol}_{\text{rxn}}$$

$$2\text{Cu}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Cu}_2\text{O}(s) \quad \Delta H^\circ = -171 \text{ kJ/mol}_{\text{rxn}}$$

49. Based on the information above, what is the value of $\Delta H^\circ$ for the following reaction?

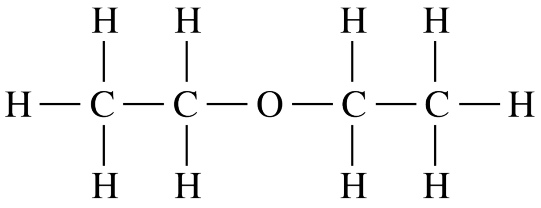
$$\text{Cu}_2\text{O}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow 2\text{CuO}(s)$$

(A) $-483$ kJ/mol$_{\text{rxn}}$

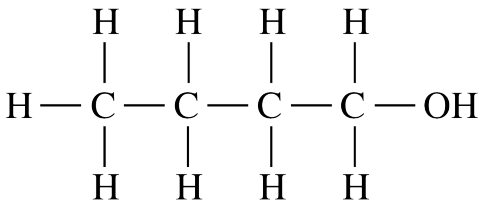
(B) $-141$ kJ/mol$_{\text{rxn}}$

(C) $+141$ kJ/mol$_{\text{rxn}}$

(D) $+483$ kJ/mol$_{\text{rxn}}$



Compound 1



Compound 2

50. The structural formulas of two compounds that are liquids at room temperature are shown above. Which of the following statements best explains the observation that compound 1 boils at 35 °C, whereas its structural isomer, compound 2, boils at 118 °C?

(A) Molecules of compound 1 have a linear shape and no net dipole, whereas molecules of compound 2 have a bent shape and are polar.

(B) Molecules of compound 1 are bent less than molecules of compound 2; thus they have weaker dipole-dipole attractions.

(C) There are dipole-dipole attractions among molecules of compound 1, whereas there are only dispersion forces among molecules of compound 2.

(D) Although there are dipole-dipole attractions among molecules of both compound 1 and compound 2, the $-$OH group in compound 2 allows strong hydrogen bonding to occur.

51. Which of the following is the best method for preparing 100.0 mL of 0.100 $M$ KCl$(aq)$?

(A) Place 74.6 g of KCl$(s)$ in a 100 mL graduated cylinder and fill to the 100.0 mL mark with water.

(B) Place 7.46 g of KCl$(s)$ in a 100 mL Erlenmeyer flask, add 92.54 g of water, and invert several times.

(C) Place 7.46 g of KCl$(s)$ in a 100 mL volumetric flask, partially fill with water, swirl flask to dissolve solid, fill to the 100.0 mL mark with water, and invert several times.

(D) Place 7.46 g of KCl$(s)$ in a 100 mL volumetric flask, partially fill with water, swirl flask to dissolve solid, add 92.54 mL of water, and invert several times.

$$2\text{NO}(g) + \text{Br}_2(g) \rightarrow 2\text{NOBr}(g)$$

52. The two mechanisms in the table below have been proposed for the reaction represented above.

| **Mechanism 1** | **Mechanism 2** |
|---|---|
| Step 1: $\text{NO}(g) + \text{NO}(g) \rightarrow \text{N}_2\text{O}_2(g)$ slow | Step 1: $\text{NO}(g) + \text{Br}_2(g) \rightarrow \text{NOBr}(g)$ slow |
| Step 2: $\text{N}_2\text{O}_2(g) + \text{Br}_2(g) \rightarrow \text{NOBr}_2(g)$ fast | Step 2: $\text{NOBr}_2(g) + \text{NO}(g) \rightarrow {}_2\text{NOBr}(g)$ fast |

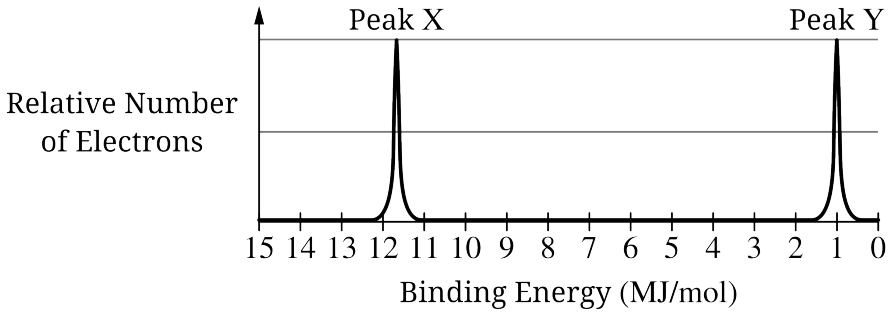
Which of the following observations would support mechanism 1 but not mechanism 2?

(A) The reaction rate is independent of [NO].

(B) The reaction rate is independent of $[\text{Br}_2]$.

(C) The reaction is exothermic.

(D) The reaction is second order overall.




53. The complete photoelectron spectrum of a pure element is represented above. Which of the following correctly identifies both the element and the atomic orbitals represented by peak X and peak Y?

| | Element | Peak X | Peak Y |
|---|---|---|---|
| (A) | Li | 1*s* | 2*s* |
| (B) | Li | 2*s* | 1*s* |
| (C) | Be | 1*s* | 2*s* |
| (D) | Be | 2*s* | 1*s* |

| Acid | p$K_a$ |
|---|---|
| $HClO_2(aq)$ | 1.92 |
| $HNO_2(aq)$ | 3.25 |
| $HC_3H_5O_2(aq)$ | 4.88 |
| $HOCl(aq)$ | 7.42 |

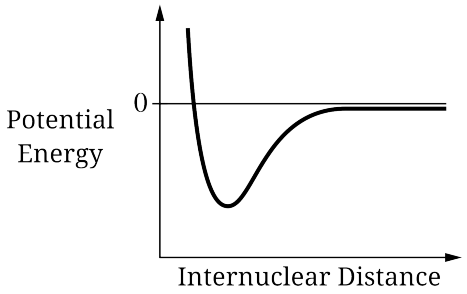
54. Based on the information in the table, which of the following mixtures forms a buffer with a pH closest to 3?

(A) 50.0 mL of 0.10 *M* $HClO_2(aq)$ and 25.0 mL of 0.10 *M* $NaOH(aq)$

(B) 50.0 mL of 0.20 *M* $HNO_2(aq)$ and 50.0 mL of 0.10 *M* $NaOH(aq)$

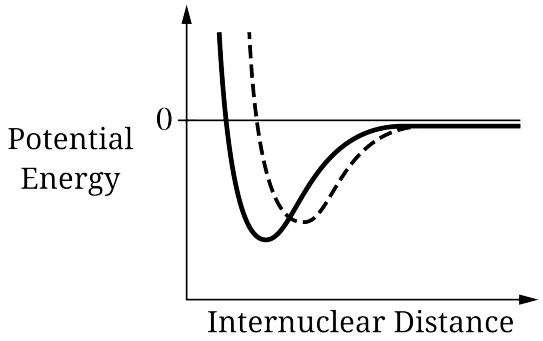
(C) 50.0 mL of 0.10 *M* $HC_3H_5O_2(aq)$ and 50.0 mL of 0.050 *M* $NaOH(aq)$

(D) 50.0 mL of 0.10 *M* $HOCl(aq)$ and 25.0 mL of 0.10 *M* $NaOH(aq)$

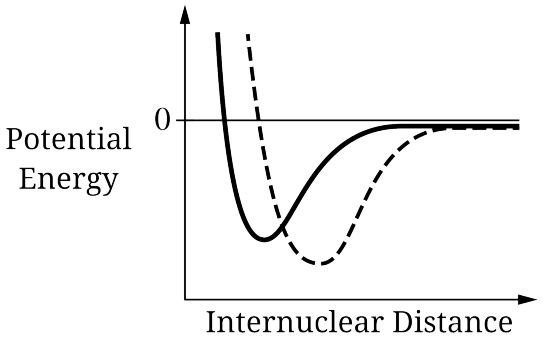



55. The graph of potential energy versus internuclear distance for the HCl molecule is shown. Which of the following graphs includes the plot for the HBr molecule, shown as a dashed line?

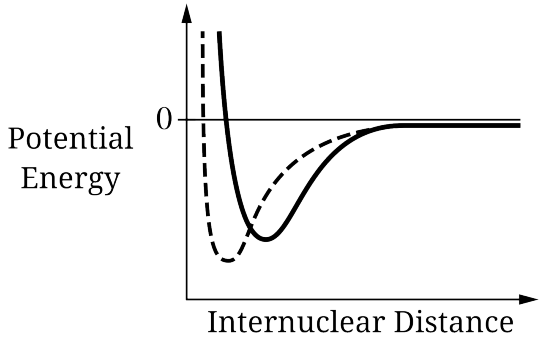
(A)



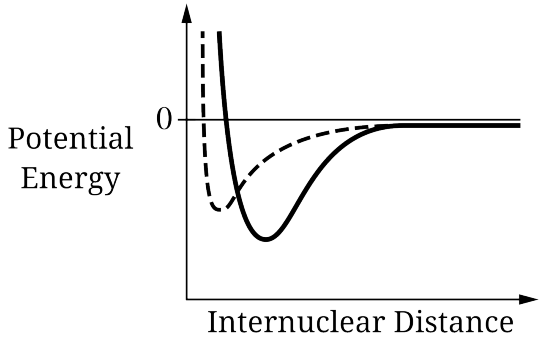

(B)




(C)

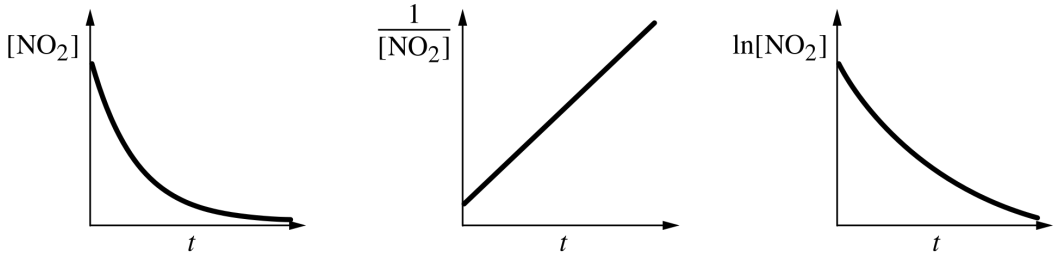



(D)



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

56. A group of students studied the rate of the reaction represented above at a fixed temperature. During the reaction, the concentration of CO was in large excess. The graphs shown below were created using the data collected by the students. Based on the graphs, which of the following is the rate law?




(A) Rate $= k$

(B) Rate $= [NO_2]$

(C) Rate $= k[NO_2]$

(D) Rate $= k[NO_2]^2$

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad K_{eq} = 240 \text{ at } 25\ ^\circ\text{C}$$

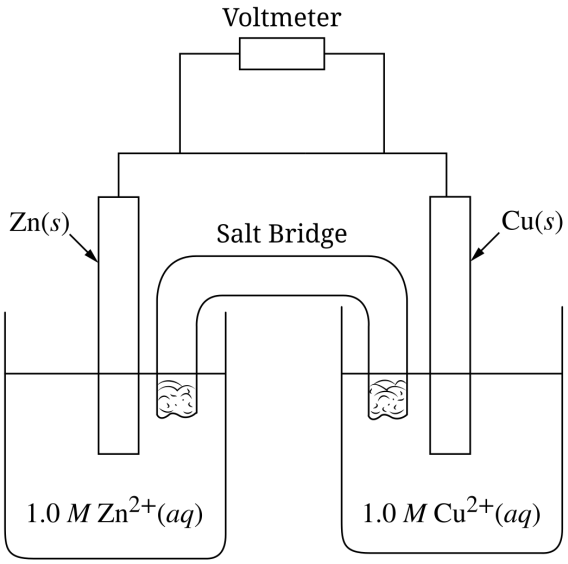
57. Equal volumes of 0.1 $M$ solutions of $Fe^{3+}(aq)$ and $SCN^-(aq)$ are mixed and allowed to attain the equilibrium represented above at a temperature of 25 °C. Which of the following statements is correct about the system at equilibrium?

(A) $[SCN^-] > [FeSCN^{2+}]$

(B) $[SCN^-] < [FeSCN^{2+}]$

(C) $[Fe^{3+}] > [FeSCN^{2+}]$

(D) $[Fe^{3+}] = [FeSCN^{2+}]$




| Half-Reaction | $E^\circ$ (V) |
|---|---|
| $Ag^+(aq) + e^- \rightarrow Ag(s)$ | 0.80 |
| $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ | 0.34 |
| $Zn^{2+}(aq) + 2e^- \rightarrow Cu(s)$ | −0.76 |

58. A student sets up a standard galvanic cell, as shown in the diagram, and measures a voltage of 1.10 V. Based on the standard reduction potentials in the table, which of the following will occur if the student makes a new standard cell but uses a silver wire in place of the salt bridge?

(A) The voltage will be greater than 1.10 V.

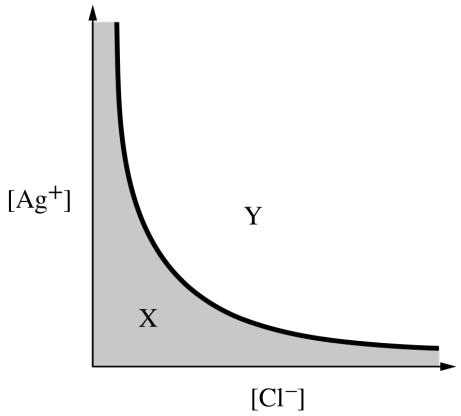
(B) The voltage will be 0.

(C) The silver wire will become thinner.

(D) $Zn(s)$ and $Cu(s)$ will form on the silver wire.

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$$

59. The preceding equation represents the equilibrium of a saturated solution of $\mathrm{AgCl}(aq)$ in contact with $\mathrm{AgCl}(s)$. All points on the curve in the following graph represent values of $[\mathrm{Ag}^{+}]$ and $[\mathrm{Cl}^{-}]$ for which the product $[\mathrm{Ag}^{+}][\mathrm{Cl}^{-}]$ is equal to the value of $K_{sp}$ for AgCl. Which of the following provides the correct comparison of $Q$ and and $K_{sp}$ describes the net process that occurs at any point in region Y(unshaded) of the graph?

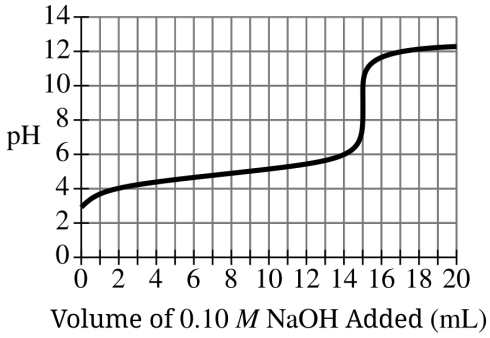



(A) $Q > K_{sp}$ and dissolution of $\mathrm{AgCl}(s)$ occurs.

(B) $Q < K_{sp}$ and dissolution of $\mathrm{AgCl}(s)$ occurs.

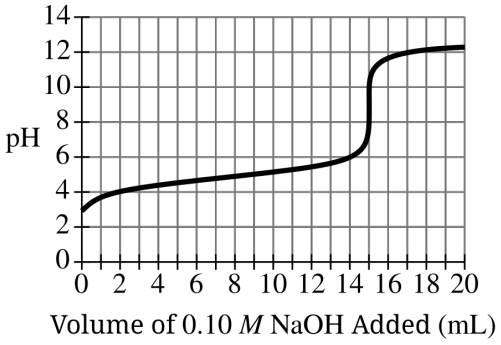
(C) $Q > K_{sp}$ and precipitation of $\mathrm{AgCl}(s)$ occurs.

(D) $Q < K_{sp}$ and precipitation of $\mathrm{AgCl}(s)$ occurs.

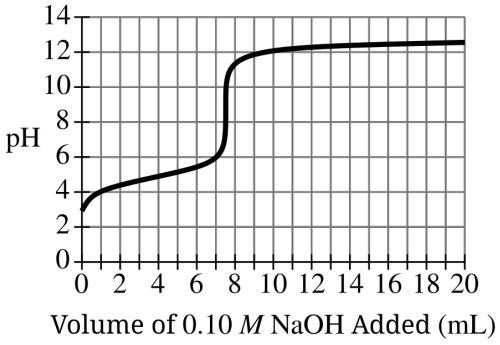



60. A 15.0 mL sample of 0.10 *M* $HC_2H_3O_2$ is titrated with 0.10 *M* NaOH, and the data are shown in the graph above. Which of the following graphs shows the change in pH when a 15.0 mL sample of 0.10 *M* HCl is titrated with 0.10 *M* NaOH?

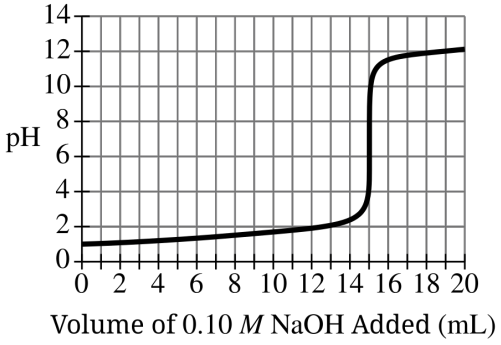
(A)



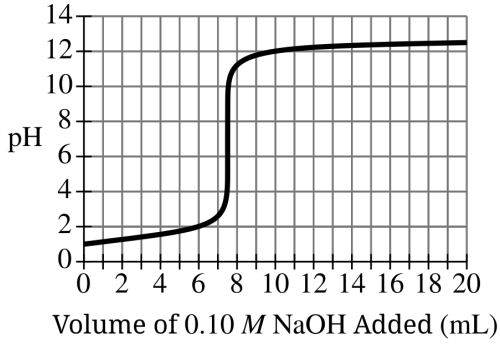

(B)




(C)




(D)




**STOP**
**END OF SECTION I**

## CHEMISTRY

## SECTION II

### Time—1 hour and 45 minutes

### 7 Questions

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

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

1. Ethanol ($C_2H_5OH$) reacts with hydrobromic acid (HBr) to produce ethyl bromide ($C_2H_5Br$) and water according to the following balanced equation.

$$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$$

(a) At the conclusion of the reaction, the product mixture includes $C_2H_5Br$, $H_2O$, and excess unreacted $C_2H_5OH$.

i. Identify all of the types of intermolecular forces that can exist between one molecule of $C_2H_5OH$ and one molecule of $C_2H_5Br$ in the product mixture.

ii. The aqueous solubility of $C_2H_5OH$ is greater than that of $C_2H_5Br$. Explain this observation based on the types and relative strengths of intermolecular forces between each solute and $H_2O$.

The reaction is found to be first order with respect to HBr when $C_2H_5OH$ is in excess. The following data were recorded showing how the concentration of HBr changes over time.

| Time (min) | 0 | 50.0 | 100.0 | 150.0 | 200.0 |
|---|---|---|---|---|---|
| [HBr] ($M$) | 2.00 | 1.80 | 1.62 | 1.46 | 1.32 |

(b) Using the data provided, calculate the value of the rate constant, $k$, in $\text{min}^{-1}$.

(c) Using the data provided, determine the half-life of the reaction, in minutes.

(d) The experiment is repeated at a higher temperature.

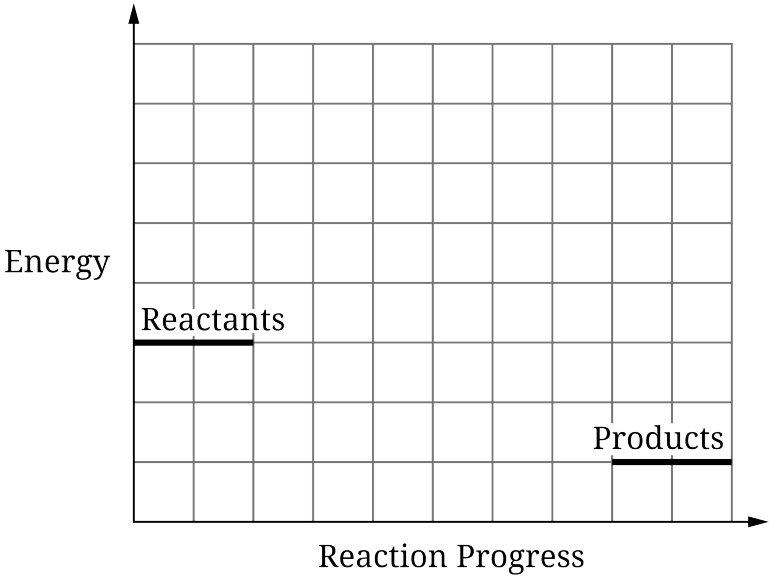
i. Explain the effect, if any, that the higher temperature has on collisions between reactant particles.

ii. Identify the effect, if any, that the higher temperature has on the rate constant. Explain your reasoning.

(e) The following reaction mechanism has been proposed for the reaction of $C_2H_5OH$ and HBr.

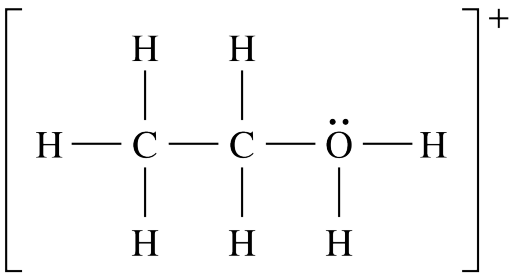
| | | | |
|---|---|---|---|
| Step 1: | $C_2H_5OH + H_3O^+ \rightleftharpoons C_2H_5OH_2^+ + H_2O$ | fast | $\Delta H_1 > 0$ |
| Step 2: | $C_2H_5OH_2^+ + Br^- \rightarrow C_2H_5Br + H_2O$ | slow | $\Delta H_2 < 0$ |
| Overall | $C_2H_5Br + H_3O^+ + Br^- \rightarrow C_2H_5Br + 2H_2O$ | | $\Delta H_{rxn} < 0$ |

i. Sketch an energy diagram that represents this reaction mechanism on the axes given.

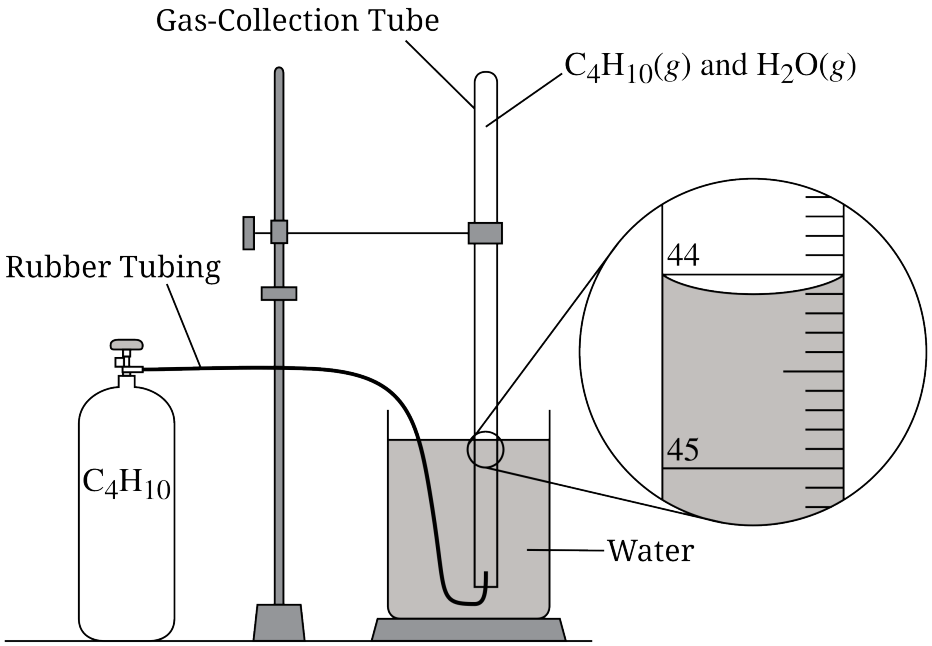



ii. In step 2 of the mechanism, only the C−O bond is broken and the C−Br bond is formed. Given that $\Delta H_2 < 0$, a student claims that more energy is needed to break the C−O bond than C−Br is released when the bond forms. Do you agree or disagree? Justify your answer.

iii. The following Lewis diagram is for the reaction intermediate, $C_2H_5OH_2^+$. On the Lewis diagram, circle an atom that has a formal charge of $+1$.



2. A student performs an experiment to determine the molar mass of butane, $C_4H_{10}$.




| | |
|---|---|
| Initial mass of $C_4H_{10}$ container | 25.012 g |
| Final mass of $C_4H_{10}$ container | 24.911 g |
| Initial volume of gas | 0.00 mL |
| Final volume of gas | ? |
| Atmospheric pressure | 0.970 atm |
| Temperature | 21.0 °C |

(a) To determine the molar mass, the student collects a sample of butane gas over water in a 50.0 mL gas-collection tube, as shown in the following diagram. The student then adjusts the position of the tube so the water level is the same inside and outside the tube. A partial data table for the experiment is also shown.

i. What should the student record for the volume of the gas collected, in mL?

ii. Given that the vapor pressure of water at 25 °C is 0.0246 atm, calculate the partial pressure, in atmospheres, of butane collected. Assume that the total pressure in the gas-collection tube is equal to the atmospheric pressure in the laboratory.

iii. Calculate the number of moles of butane gas in the gas-collection tube.

(b) The student then incorrectly determines the molar mass of butane by dividing the initial mass of the container with butane (25.012 g) by the number of moles of butane calculated in part (a)(iii). Assuming that the number of moles calculated in part (a)(iii) is accurate, describe how to correct the student's calculation.

Butane undergoes combustion according to the following balanced equation.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) \qquad \Delta H^\circ = -2660 \text{ kJ/mol}_{\text{rxn}}$$

(c) Which species undergoes reduction in the combustion reaction? Justify your answer with oxidation numbers.

(d) Determine the sign of the entropy change for the reaction. Use particle reasoning to justify your answer.

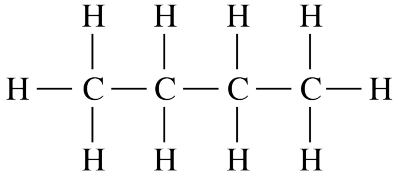
(e) A student combusts $9.29 \times 10^{-4}$ mol of butane as shown in the preceding equation in a calorimeter containing 100.0 g of water.

i. Calculate the heat, in J, released during the combustion of butane.

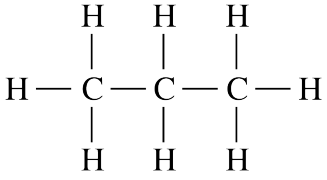
ii. Calculate the temperature change of the water in the calorimeter. (Assume that the calorimeter is perfectly insulated and all the heat released by the combustion of butane is transferred to the 100.0 g sample of water.) The specific heat capacity of water is 4.18 J/(g·°C).

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g) \qquad \Delta H^\circ = -2040 \text{ kJ/mol}_{\text{rxn}}$$

(f) Predict whether the change in temperature observed during the combustion would be greater than, less than, or equal to the change in part (e)(ii). Justify your answer.



Butane

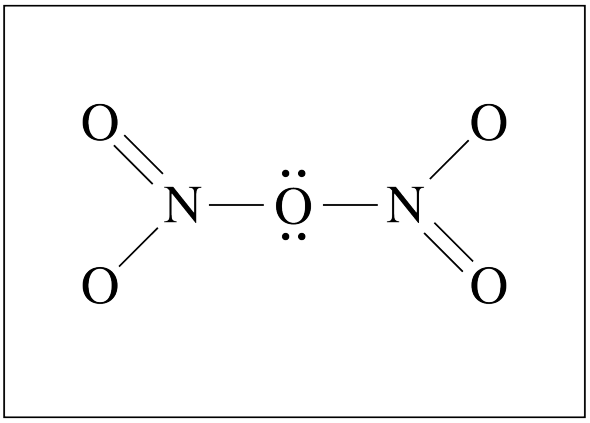


Propane

(g) The Lewis diagrams for butane and propane are shown above. Both compounds exhibit London dispersion attractive forces. Explain why the London dispersion forces between molecules of butane are stronger than those between molecules of propane.

3. Answer the following questions related to $N_2O_5$ and $H_2NO_3$.

   (a) An incomplete Lewis diagram for $N_2O_5$ is shown. Draw all of the remaining nonbonding electrons on the diagram.




   (b) Based on VSEPR theory and the molecular geometry around the central O atom, what is the predicted N−O−N bond angle?

   When $N_2O_5(g)$ is added to water, $HNO_3(aq)$ is formed according to the following equation.

$$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(aq)$$

   Thermodynamic data for the reaction at 298 K are given in the following table.

| | |
|---|---|
| $\Delta H^\circ$ | $-140$ kJ/mol$_{rxn}$ |
| $\Delta S^\circ$ | $-124$ J/(K·mol$_{rxn}$) |

   (c) Calculate the value of $\Delta G^\circ$, in kJ/mol$_{rxn}$, at 298 K.

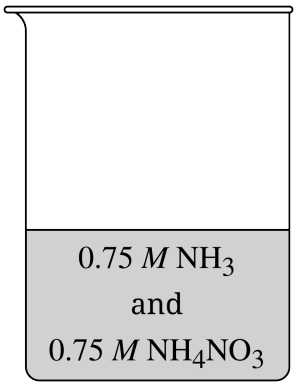
   (d) A student claims that lowering the temperature makes the value of $\Delta G^\circ$ more negative. Do you agree or disagree? Justify your answer.

$$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(aq)$$

(e) Enough $N_2O_5(g)$ is added to distilled water to make 350.0 mL of $HNO_3(aq)$, as shown in the preceding equation. The resulting solution has pH a of 1.62.

i. Calculate the value of $[H_3O^+]$ in the solution.

ii. Assuming the $HNO_3(aq)$ is produced with 100% yield, calculate the mass of $N_2O_5(g)$ (molar mass 108.02 g/mol) that was added in part (e).




100.0 mL

(f) A buffer solution is prepared in a beaker as shown. Calculate the pH of the solution in the beaker. The $K_a$ of $NH_4^+$ is $5.6 \times 10^{-10}$.

(g) Four students are each given a different beaker containing 100.0 mL of a solution that contains 0.75 *M* $NH_3$ and 0.75 *M* $NH_4NO_3$. Each student adds a different amount of 1.0 *M* $HNO_3$ and then correctly measures the pH of their solution, as shown in the following table.

| Student | Volume of Buffer (mL) | Amount of $HNO_3$ Added (mL) | pH after $HNO_3$ Addition |
|---|---|---|---|
| A | 100.0 | 20 | 9.01 |
| B | 100.0 | 40 | 8.73 |
| C | 100.0 | 60 | 8.30 |
| D | 100.0 | 80 | 1.56 |

i. Write a balanced net ionic equation for the reaction that occurs when a small amount of $HNO_3$ is added to Student A's buffer solution.

ii. What evidence in the data table indicates that the buffer capacity is exceeded only in the solution prepared by Student D?

4. Answer the following questions about atomic structure and bonding.

   (a) Write the complete ground-state electron configuration of the Kr atom.

   (b) The $Rb^+$ ion has the same electron configuration as the neutral Kr atom. Which has the larger radius, the $Rb^+$ ion or the Kr atom? Justify your answer in terms of Coulomb's law.

   (c) The composition of a sample of solid Rb containing a high percentage of the radioactive isotope Rb-83 is given in the following table.

| Isotope | Isotopic Mass (amu) | Percentage of Sample | Isotope Half-Life |
|---|---|---|---|
| Rb-83 | 82.92 | 32.5% | 86 days |
| Rb-85 | 84.91 | 50.8% | stable |
| Rb-87 | 86.91 | 16.7% | stable |

   i. Using the values in the table, calculate the average atomic mass, in amu, of Rb in the sample.

   ii. Rb-83 undergoes radioactive decay into gaseous Kr-83, which leaves the solid sample. Over time, how will the average atomic mass of the remaining sample compare to the value calculated in part (c)(i)?

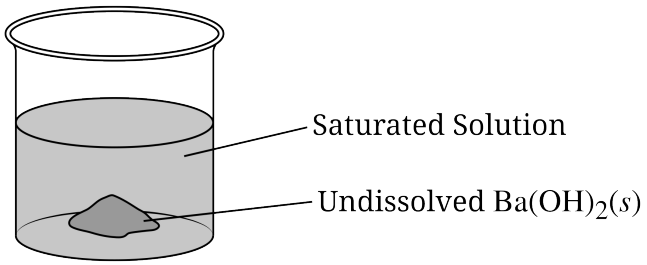
5. To determine the value of the solubility product constant, $K_{sp}$, a student prepares a saturated solution by dissolving $Ba(OH)_2(s)$ in water. The $K_{sp}$ expression is $K_{sp} = [Ba^{2+}][OH^-]^2$.

   (a) Write the balanced equation for the dissociation reaction that is consistent with the $K_{sp}$ expression.

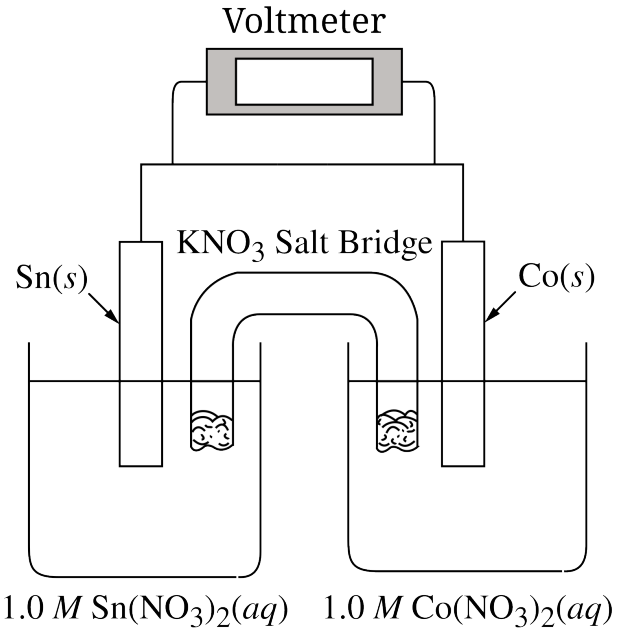
   (b) The student determines that the solubility of $Ba(OH)_2(s)$ is 18.5 g/L at 25 °C.

      i. Calculate the molar solubility of $Ba(OH)_2(s)$ in mol/L at 25 °C.

      ii. Calculate the value of $K_{sp}$ for $Ba(OH)_2(s)$ at 25 °C.




   (c) The student creates a saturated solution of $Ba(OH)_2$ in water, as shown in the diagram. The student claims that the amount of undissolved $Ba(OH)_2(s)$ will decrease when $HNO_3(aq)$ is added. Do you agree or disagree with the student's claim? Justify your answer with a comparison of $Q$ and $K_{sp}$.




6. A student sets up a galvanic cell with one half-cell made with a tin electrode and a $Sn^{2+}$ solution and the second half-cell made with a cobalt electrode and a $Co^{2+}$ solution, as shown. The salt bridge contains $KNO_3(aq)$.

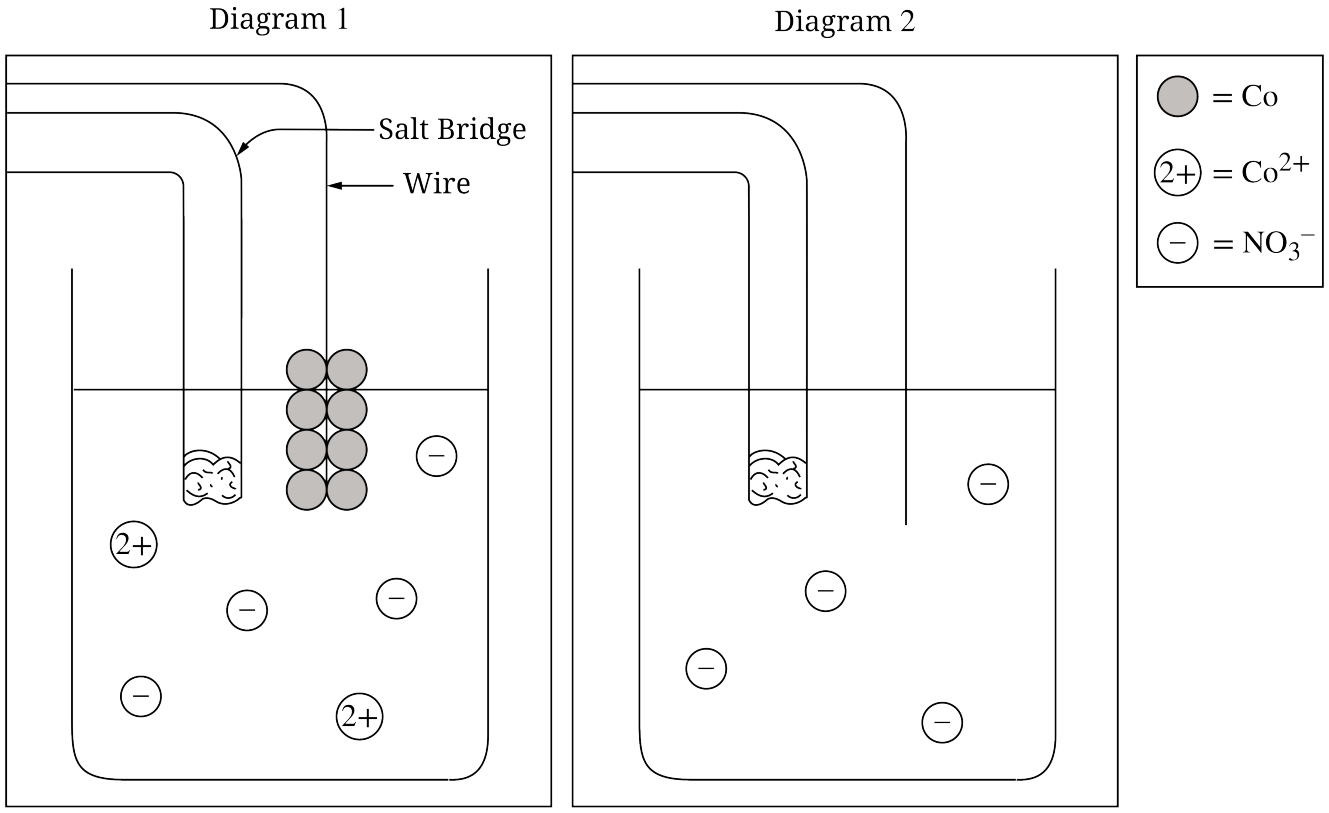
   (a) The following table provides standard reduction potentials.

| Half-Reaction | $E^\circ$ (V) |
|---|---|
| $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ | $-0.138$ |
| $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$ | $-0.277$ |

   i. Given the balanced equation $Sn^{2+} + Co \rightarrow Sn + Co^{2+}$, determine the standard cell potential, $E^\circ_{cell}$.

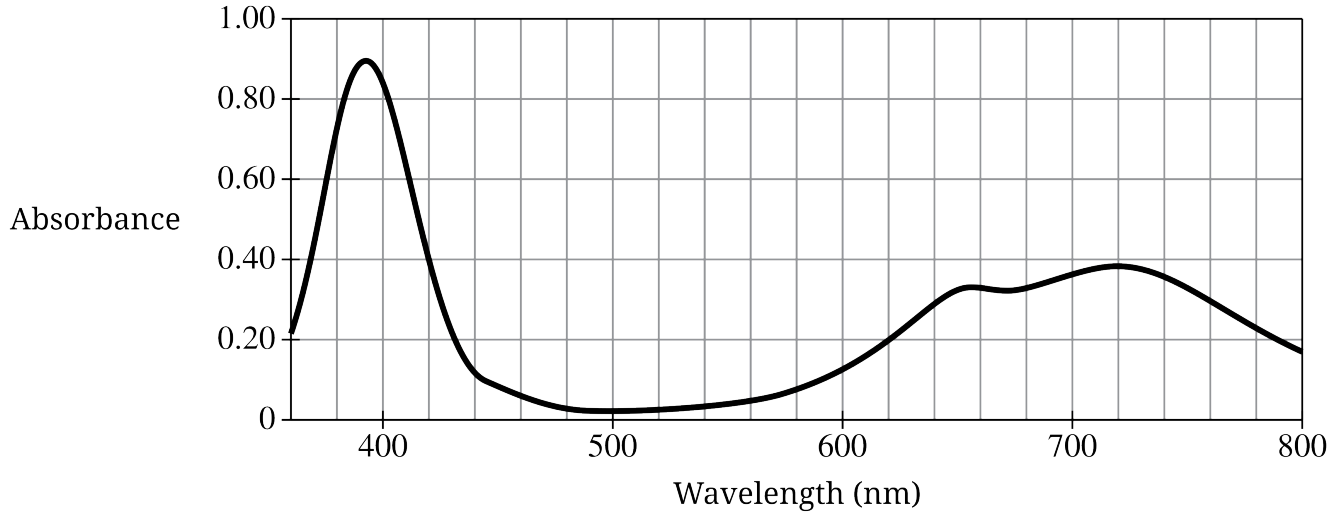
   ii. Is the value of $\Delta G^\circ$ for the overall electrochemical reaction greater than, less than, or equal to zero? Justify your answer based on the value of $E^\circ_{cell}$.

(b) A representation of the cobalt half-cell before the reaction starts is shown in diagram 1. The student observes that as the cell operates, the solution becomes a darker shade of pink. In diagram 2, complete the representation of the cobalt half-cell after the cell has operated for a short time. Be sure that mass is conserved. The balance of charge is not necessary, and all species may not need to be shown in the drawing.



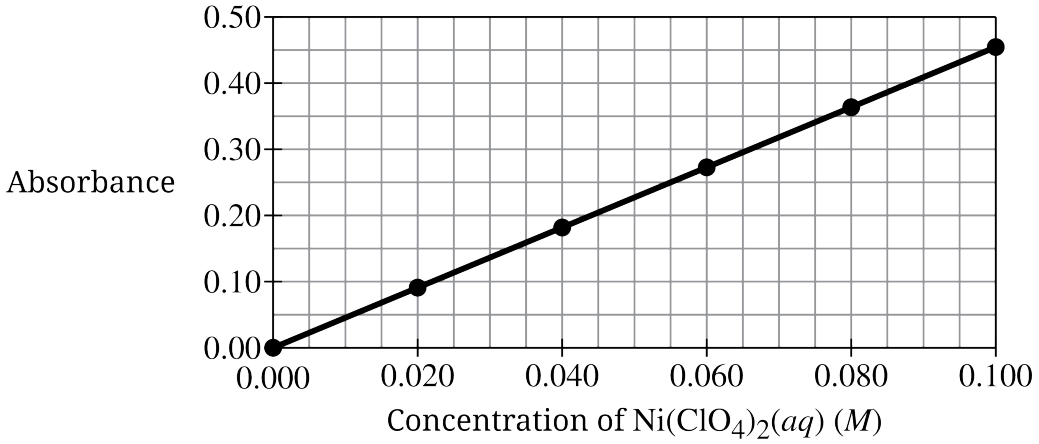

(c) A second galvanic cell is constructed such that $[Sn^{2+}] = 1.0\ M$ and $[Co^{2+}] = 0.20\ M$. How does the cell potential of this second galvanic cell compare to the cell potential of the first cell?

7. A student performs a spectrophotometry experiment using solutions of $Ni(ClO_4)_2(aq)$. The student needs to make a standard curve and determine the concentration of $Ni(ClO_4)_2(aq)$ in a sample with an unknown concentration.

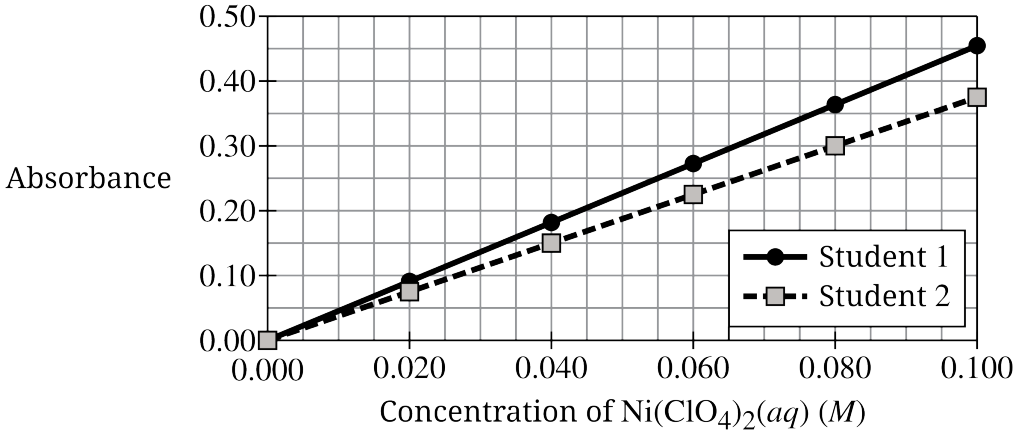



(a) Based on the absorbance spectrum of $Ni(ClO_4)_2(aq)$ shown in the preceding graph, what wavelength should the student use in the experiment to achieve the greatest precision?

(b) To make the standard curve, the student must prepare $Ni(ClO_4)_2(aq)$ solutions with different concentrations. The student has a standard solution of $Ni(ClO_4)_2(aq)$ with a concentration of 0.198 $M$. Calculate the volume, in mL, of 0.198 $M$ $Ni(ClO_4)_2(aq)$ that is needed to prepare 250.0 mL of 0.0400 $M$ $Ni(ClO_4)_2(aq)$.




(c) The standard curve generated by the student is provided above. The student measures an absorbance of 0.30 for the unknown solution. Using the standard curve provided, determine the molarity of $Ni(ClO_4)_2(aq)$ in the unknown solution.




(d) A second student repeats the procedure using the same spectrophotometer but makes an error, which results in the dashed line shown in the graph above. Assuming that the first student's data (shown by the solid line) are correct, identify one error that could account for the second student's standard curve being less steep than that obtained by the first student.

**STOP**
**END OF EXAM**