CHEMISTRY

Section I

Time—1 hour and 30 minutes

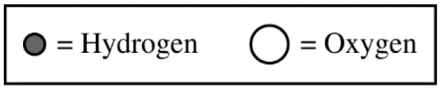
50 Questions

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. Which of the following particle diagrams best represents the products when four molecules of $H_2O_2(l)$ decompose into water and oxygen gas at room temperature?



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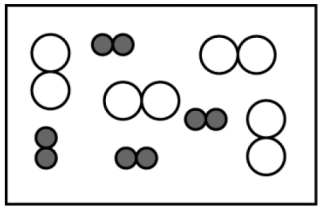

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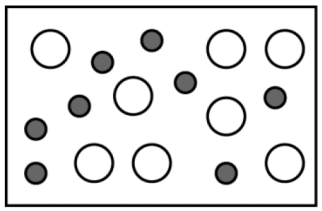

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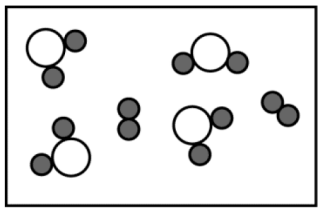

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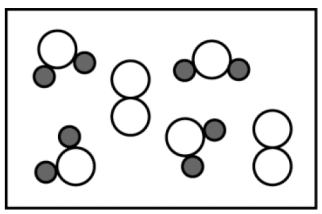

Sample	Mass of Carbon	Mass of Hydrogen
A	60. g	12 g
B	72 g	12 g
C	84 g	10. g
D	90. g	10. g

2. The masses of carbon and hydrogen in samples of four pure hydrocarbons are given above. The hydrocarbon in which sample has the same empirical formula as propene, C_3H_6 ?

(A) Sample A
(B) Sample B
(C) Sample C
(D) Sample D

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Substance	X	Y	Z
Melting Point (°C)	1600	650	1418
Electrical Conductivity in Solid Phase	None	High	None
Electrical Conductivity in Liquid Phase	None	High	High

3. Three substances were studied in the laboratory, and the data in the table above were collected. Based on the data, which of the following shows the type of bonding in each substance?

	Substance X	Substance Y	Substance Z
(A)	Network covalent	Ionic	Metallic
(B)	Ionic	Molecular	Network covalent
(C)	Molecular	Network covalent	Metallic
(D)	Network covalent	Metallic	Ionic

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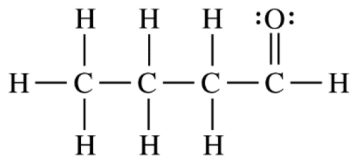
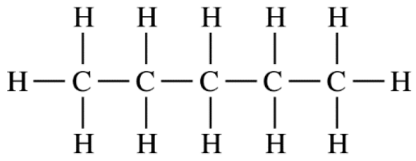
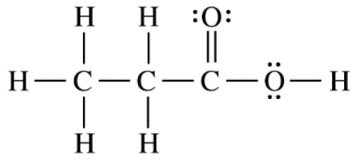
Compound Name	Structural Formula	Molar Mass (g/mol)
Butanal		72.10
Pentane		72.15
Propanoic acid		74.08

4. Based on the information in the table above, which of the compounds has the highest boiling point, and why?

(A) Butanal, because it can form intermolecular hydrogen bonds
(B) Pentane, because it has the longest carbon chain
(C) Pentane, because it has the most C–H bonds
(D) Propanoic acid, because it can form intermolecular hydrogen bonds

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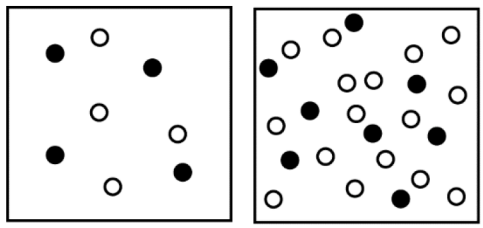
5. A 1.0 L sample of a pure gas is found to have a lower pressure than that predicted by the ideal gas law. The best explanation for the observation is that the molecules of the gas

   (A) have a combined volume that is too large to be considered negligible when compared to the volume of the container
   (B) have a low molecular mass and therefore do not strike the container walls with as much force as expected
   (C) are attracted to each other and do not exert as much force on the container walls as they would if they had no mutual attractions
   (D) are attracted to the sides of the container and strike the container walls with more force than expected



Key
● Any positive ion
○ Any negative ion

H_2O molecules are not shown.

6. Equal volumes of solutions in two different vessels are represented above. If the solution represented in vessel 1 is KCl(*aq*), then the solution represented in vessel 2 could be an aqueous solution of

   (A) KCl with the same molarity as the solution in vessel 1
   (B) KCl with twice the molarity of the solution in vessel 1
   (C) $CaCl_2$ with the same molarity as the solution in vessel 1
   (D) $CaCl_2$ with twice the molarity of the solution in vessel 1

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7. A 20. mL sample of 0.50 *M* $HC_2H_3O_2(aq)$ is titrated with 0.50 *M* NaOH(*aq*). Which of the following best represents the species that react and the species produced in the reaction?

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

(B) $H^+(aq) + C_2H_3O_2^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow H_2O(l) + NaC_2H_3O_2(aq)$

(C) $HC_2H_3O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$

(D) $HC_2H_3O_2(aq) + NaOH(aq) \rightarrow H_2O(l) + Na^+(aq) + C_2H_3O_2^-(aq)$

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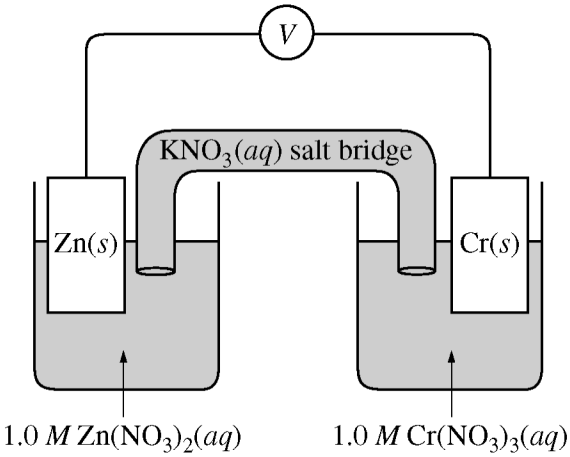

8. The standard reduction potentials for the half-reactions related to the galvanic cell represented above are listed in the table below.

Half-Reaction	E° (V)
$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76

Which of the following gives the value of E°_{cell} for the cell?

(A) $E^\circ_{cell} = -1.50$ V

(B) $E^\circ_{cell} = -0.80$ V

(C) $E^\circ_{cell} = -0.02$ V

(D) $E^\circ_{cell} = +0.02$ V

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	Ionization Energy (kJ/mol)
First	730
Second	1450
Third	7700
Fourth	10,500

9. The ionization energies of an unknown element, X, are listed in the table above. Which of the following is the most likely empirical formula of a compound formed from element X and phosphorus, P ?

(A) XP
(B) X_3P
(C) X_3P_2
(D) X_3P_4

10. Which of the following correctly compares periodic properties of two elements and provides an accurate explanation for that difference?

(A) The first ionization energy of Al is greater than that of B because Al has a larger nuclear charge than B does.
(B) The first ionization energy of F is greater than that of O because O has a higher electronegativity than F has.
(C) The atomic radius of Ca is larger than that of Mg because the valence electrons in Mg experience more shielding than the valence electrons in Ca do.
(D) The atomic radius of Cl is smaller than that of S because Cl has a larger nuclear charge than S does.

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$$HNO_2(aq) \rightleftarrows H^+(aq) + NO_2^-(aq) \qquad K_a = 4.0 \times 10^{-4}$$

11. On the basis of the information above, what is the approximate percent ionization of HNO_2 in a 1.0 M $HNO_2(aq)$ solution?

(A) 0.00040%
(B) 0.020%
(C) 0.040%
(D) 2.0%

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$$2\ NOBr(g) \rightarrow 2\ NO(g) + Br_2(g)$$

12. The equation above represents an elementary step in a chemical reaction. Which of the following is the correct expression for the rate law of the elementary step?

(A) Rate = $k[NOBr]^{\frac{1}{2}}$

(B) Rate = $k[NOBr]$

(C) Rate = $k[NOBr]^2$

(D) Rate = $k[NO]^2[Br_2]$

13. A balloon filled with 0.25 mol of $He(g)$ at 273 K and 1 atm is allowed to rise through the atmosphere. Which of the following explains what happens to the volume of the balloon as it rises from ground level to an altitude where the air temperature is 220 K and the air pressure is 0.1 atm?

(A) The volume will increase because the decrease in air pressure will have a greater effect than the decrease in temperature.

(B) The volume will remain unchanged because of the counteracting effects of the decrease in temperature and the decrease in air pressure.

(C) The volume will decrease because the decrease in temperature will have a greater effect than the decrease in air pressure.

(D) It cannot be determined whether the volume of the balloon will increase, decrease, or remain the same without knowing the initial volume of the balloon.

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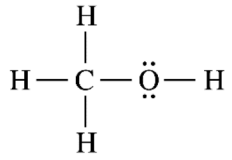
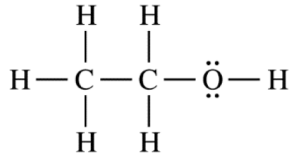
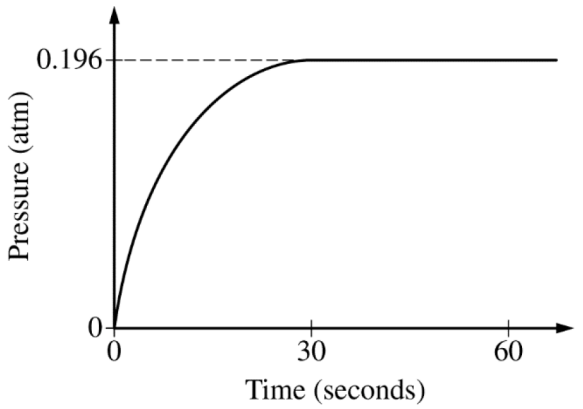
Questions 14-17 refer to the following information.

Substance	Lewis Diagram	Boiling Point
CH_3OH		338 K
C_2H_5OH		351 K

Equimolar samples of $CH_3OH(l)$ and $C_2H_5OH(l)$ are placed in separate, previously evacuated, rigid 2.0 L vessels. Each vessel is attached to a pressure gauge, and the temperatures are kept at 300 K. In both vessels, liquid is observed to remain present at the bottom of the container at all times. The change in pressure inside the vessel containing $CH_3OH(l)$ is shown below.



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14. Which of the following best describes the change that takes place immediately after the $CH_3OH(l)$ is introduced into the previously evacuated vessel?

(A) A chemical change takes place because covalent bonds are broken.
(B) A chemical change takes place because intermolecular attractions are overcome.
(C) A physical change takes place because covalent bonds are broken.
(D) A physical change takes place because intermolecular attractions are overcome.

15. The value of K_p for the evaporation of $CH_3OH(l)$ at 300 K is closest to

(A) 0.04
(B) 0.2
(C) 5
(D) 30

16. The temperature of the CH_3OH is increased from 300 K to 400 K to vaporize all the liquid, which increases the pressure in the vessel to 0.30 atm. The experiment is repeated under identical conditions but this time using half the mass of CH_3OH that was used originally. What will be the pressure in the vessel at 400 K ?

(A) 0.15 atm
(B) 0.30 atm
(C) 0.40 atm
(D) 0.60 atm

17. Compared to the equilibrium vapor pressure of $CH_3OH(l)$ at 300 K, the equilibrium vapor pressure of $C_2H_5OH(l)$ at 300 K is

(A) the same, because both compounds have hydrogen bonding among their molecules
(B) higher, because London dispersion forces among C_2H_5OH molecules are greater than those among CH_3OH molecules
(C) lower, because London dispersion forces among C_2H_5OH molecules are greater than those among CH_3OH molecules
(D) lower, because of the larger number of hydrogen bonds among C_2H_5OH molecules

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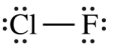
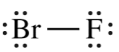
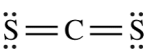
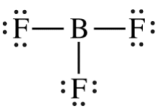
18. Which of the following Lewis electron-dot diagrams represents the molecule that is the most polar?

(A) 

(B) 

(C) 

(D) 

Ion	Ionic Radius (pm)
Cl^-	181
I^-	216
S^{2-}	184
Te^{2-}	221

19. Based on Coulomb's law and the information in the table above, which of the following anions is most likely to have the strongest interactions with nearby water molecules in an aqueous solution?

(A) Cl^-
(B) I^-
(C) S^{2-}
(D) Te^{2-}

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20. For which of the equilibrium systems represented below will the amount of products) at equilibrium increase if the volume of the reaction vessel is increased at a constant temperature?

(A) $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$

(B) $2\ NO(g) + O_2(g) \rightleftarrows 2\ NO_2(g)$

(C) $N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$

(D) $2\ CO(g) \rightleftarrows C(s) + CO_2(g)$

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

21. In an experiment a student mixes a 50.0 mL sample of 0.100 *M* $AgNO_3(aq)$ with a 50.0 mL sample of 0.100 *M* $NaCl(aq)$ at 20.0°C in a coffee-cup calorimeter. Which of the following is the enthalpy change of the precipitation reaction represented above if the final temperature of the mixture is 21.0°C? (Assume that the total mass of the mixture is 100. g and that the specific heat capacity of the mixture is 4.2 J/(g·°C).)

(A) $-84\ kJ/mol_{rxn}$

(B) $-0.42\ kJ/mol_{rxn}$

(C) $0.42\ kJ/mol_{rxn}$

(D) $84\ kJ/mol_{rxn}$

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Questions 22-24 refer to the following information.

A group of students was asked to recover $Cu(s)$ from a blue-green aqueous solution containing an unknown concentration of $Cu^{2+}(aq)$. The students took a 100.0 mL sample of the solution and added an excess of 1.0 *M* $Na_3PO_4(aq)$, causing the $Cu^{2+}(aq)$ to precipitate as $Cu_3(PO_4)_2(s)$, as shown in step 1 below.

Step 1



Blue-green $Cu^{2+}(aq)$ + Colorless 1.0 *M* $Na_3PO_4(aq)$ → Blue-green $Cu_3(PO_4)_2(s)$

$$3\ Cu^{2+}(aq) + 2\ Na_3PO_4\ (aq) \longrightarrow Cu_3(PO_4)_2(s) + 6\ Na^{+}(aq)$$

The $Cu_3(PO_4)_2(s)$ was filtered, dried, and weighed. Then the $Cu_3(PO_4)_2(s)$ was dissolved in a 3.0 *M* $HCl(aq)$ solution, as shown in step 2 below.

Step 2

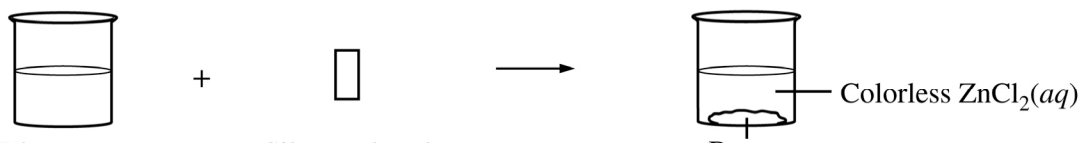


Blue-green $Cu_3(PO_4)_2(s)$ + Colorless 3.0 *M* $HCl(aq)$ → Blue-green $CuCl_2(aq) + H_3PO_4(aq)$

$$Cu_3(PO_4)_2(s) + 6\ HCl(aq) \longrightarrow 3\ CuCl_2(aq) + 2\ H_3PO_4(aq)$$

The students added a strip of $Zn(s)$ to the solution to recover the $Cu(s)$, as shown in step 3 below.

Step 3



Blue-green $CuCl_2(aq)$ + Silver-colored $Zn(s)$ → Brown $Cu(s)$

$$CuCl_2(aq) + Zn(s) \longrightarrow Cu(s) + ZnCl_2(aq)$$

Finally, the Cu(s) was filtered, dried, and weighed.

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22. If 3.8 g of $Cu_3(PO_4)_2(s)$ was recovered from step 1, what was the approximate $[Cu^{2+}]$ in the original solution? (The molar mass of $Cu_3(PO_4)_2$ is 381 g/mol.)

(A) 0.10 *M*
(B) 0.30 *M*
(C) 1.0 *M*
(D) 3.0 *M*

23. The mass of the $Cu(s)$ produced in step 3 was slightly more than the mass predicted from the 3.8 g of $Cu_3(PO_4)_2(s)$ recovered from step 1. Which of the following could account for the discrepancy in the yield of $Cu(s)$ from step 3 ?

(A) All of the $Cu_3(PO_4)_2(s)$ dissolved in the $HCl(aq)$.
(B) Some of the Cu(s) adhered to the side of the funnel used to filter the solution.
(C) Some unreacted Zn(s) was mixed in with the $Cu(s)$.
(D) Too much $Na_3PO_4(aq)$ was added to the original $Cu^{2+}(aq)$ solution.

$H_3PO_4(aq)$	
K_{a_1}	7.5×10^{-3}
K_{a_2}	6.2×10^{-8}
K_{a_3}	4.2×10^{-13}

24. The values of the dissociation constants for H_3PO_4 are given in the table above. Given that the solution in the beaker at the end of step 2 had a pH of approximately 1, which of the following chemical species had the lowest concentration among the products of step 2 ?

(A) $H^+(aq)$
(B) $H_2PO_4^-(aq)$
(C) $HPO_4^{2-}(aq)$
(D) $PO_4^{3-}(aq)$

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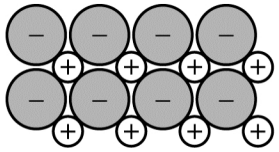

25. Which of the following most likely describes the solid represented in the diagram above?

(A) It is soft and is a poor thermal and electrical conductor.

(B) It has a low melting point and is a poor thermal and electrical conductor as a solid.

(C) It is a brittle, water-soluble electrolyte that is a poor thermal and electrical conductor as a solid.

(D) It is malleable and is an excellent thermal and electrical conductor as a solid.

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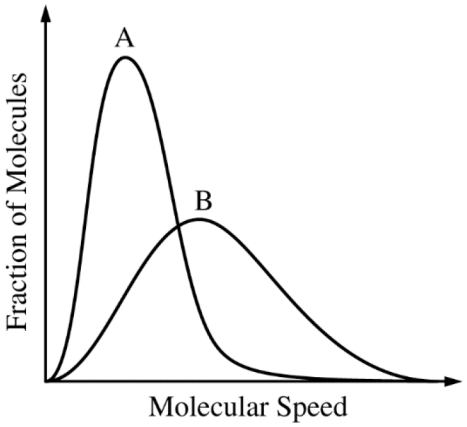
26. Which of the following best helps to explain why CCl_4 is a liquid whereas CI_4 is a solid when both are at 25°C?

(A) The dipole moment of the CCl_4 molecule is larger than that of the CI_4 molecule because Cl is more electronegative than I.

(B) The dipole moment of the CIs molecule is larger than that of the CCl molecule because there is stronger repulsion between electrons in the C–I bonds compared to the repulsion between electrons in the C–Cl bonds.

(C) The London dispersion forces are stronger in CCl_4 than in CI_4 because Cl is more electronegative than I.

(D) The London dispersion forces are stronger in CI_4 than in CCl_4 because CI_4 has a more polarizable electron cloud than CCl_4.



27. The Maxwell-Boltzmann distributions of molecular speeds in samples of two different gases at the same temperature are shown above. Which gas has the greater molar mass?

(A) Gas A
(B) Gas B
(C) Both gases have the same molar mass.
(D) It cannot be determined unless the pressure of each sample is known.

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$$CaF_2(s) \rightleftarrows Ca^{2+}(aq) + 2\,F^-(aq) \qquad \Delta H > 0$$

28. Dissolution of the slightly soluble salt CaF_2 is shown by the equation above. Which of the following changes will decrease $[Ca^{2+}]$ in a saturated solution of CaF_2, and why? (Assume that after each change some $CaF_2(s)$ remains in contact with the solution.)

(A) Allowing some of the water to evaporate from the solution, because more $CaF_2(s)$ will precipitate

(B) Adding 0.1 *M* $HNO_3(aq)$, because some $F^-(aq)$ ions will become protonated

(C) Adding 0.1 *M* $NaNO_3(aq)$, because additional liquid will dilute the solution

(D) Adding $NaF(s)$, because the reaction will proceed toward reactants

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Compound	K_{sp} at 25°C
$Pb(OH)_2(s)$	1.2×10^{-15}
$PbI_2(s)$	1.4×10^{-8}
$PbF_2(s)$	4.0×10^{-8}

29. Equimolar samples of $Pb(OH)_2(s)$, $PbI_2(s)$, and $PbF_2(s)$ are placed in three separate beakers, each containing 250 mL of water at 25°C. After the solutions are stirred, solid remains in the bottom of each beaker. Based on the K_{sp} values for the compounds listed in the table above, a solution of which of the compounds will have the lowest $[Pb^{2+}]$?

(A) $Pb(OH)_2(s)$

(B) $PbI_2(s)$ only

(C) $PbF_2(s)$ only

(D) Both $PbI_2(s)$ and $PbF_2(s)$ will produce solutions with the same, lowest $[Pb^{2+}]$.

30. When a small amount of 12 *M* $HNO_3(aq)$ is added to a butter solution made by mixing $CH_3NH_2(aq)$ and $CH_3NH_3Cl(aq)$, the pH of the buffer solution changes from 10.64 to 10.62. Which of the following equations represents the reaction that accounts for the fact that the pH does not change significantly when the $HNO_3(aq)$ is added?

(A) $CH_3NH_2(aq) + H^+(aq) \rightarrow CH_3NH_3^+(aq)$

(B) $CH_3NH_3^+(aq) + H^+(aq) \rightarrow CH_3NH_4^{2+}(aq)$

(C) $NO_3^-(aq) + H^+(aq) \rightarrow HNO_3(aq)$

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

---

31. The pH of a solution made by combining 150.0 mL of 0.10 *M* $KOH(aq)$ with 50.0 mL of 0.20 *M* $HBr(aq)$ is closest to which of the following?

(A) 2
(B) 4
(C) 7
(D) 12

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Step 1: $H_2SeO_3(aq) \rightleftarrows HSeO_3^-(aq) + H^+(aq)$ $\quad K_{a_1} = 2.1 \times 10^{-3}$

Step 2: $HSeO_3^-(aq) \rightleftarrows SeO_3^{2-}(aq) + H^+(aq)$ $\quad K_{a_2} = 5.3 \times 10^{-9}$

32. The step-wise dissociation of selenous acid, $H_2SeO_3(aq)$, is represented by the equations above. Which of the following best helps explain why the value of K_{a_2} is so much smaller than the value of K_{a_1}?

(A) The Se atom in $H_2SeO_3(aq)$ is in a higher oxidation state than the Se atom in $HSeO_3^-(aq)$.

(B) Water is more attracted to $HSeO_3^-(aq)$ ions than to SeO_3^{2-} ions, which drives the step 2 equilibrium toward the reactant.

(C) The $HSeO_3^-(aq)$ ions produced in step 1 are asymmetrical, but the SeO_3^{2-} ions produced in step 2 are symmetrical.

(D) Removing the first H^+ from $H_2SeO_3(aq)$ requires less energy than removing the second H^+, because the second Ht is removed from a negatively charged species.

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Questions 33-36 refer to the following information.

$$Li_3N(s) + 2\ H_2(g) \rightleftarrows LiNH_2(s) + 2\ LiH(s) \qquad \Delta H^\circ = -192\ \text{kJ/mol}_{rxn}$$

Because pure H_2 is a hazardous substance, safer and more cost effective techniques to store it as a solid for shipping purposes have been developed. One such method is the reaction represented above, which occurs at 200°C.

33. When 70. g of $Li_3N(s)$ (molar mass 35 g/mol) reacts with excess $H_2(g)$, 8.0 g of $LiH(s)$ is produced. The percent yield is closest to

(A) 17%
(B) 25%
(C) 50.%
(D) 100%

34. Which of the following happens to H atoms in the forward reaction?

(A) H atoms are oxidized only.
(B) H atoms are reduced only.
(C) H atoms are both oxidized and reduced.
(D) H atoms are neither oxidized nor reduced.

35. Which of the following is the most likely reason that the reaction occurs at a significant rate only if the temperature of the reaction mixture is greater than 200°C?

(A) The reaction is exothermic.
(B) ΔS° for the reaction is negative.
(C) The reaction has a high activation energy.
(D) $\Delta G^\circ < 0$ when $T < 200°C$.

36. The amount of $H_2(g)$ present in a reaction mixture at equilibrium can be maximized by

(A) increasing the temperature and increasing the pressure by decreasing the volume
(B) increasing the temperature and decreasing the pressure by increasing the volume
(C) decreasing the temperature and increasing the pressure by decreasing the volume
(D) decreasing the temperature and decreasing the pressure by increasing the volume

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$$H_2(g) + I_2(g) \rightleftarrows 2\ HI(g) \qquad K_c = 50.\ \text{at } 600°C$$

37. Equimolar samples of each of three gases, $H_2(g)$, $I_2(g)$, and $HI(g)$, are introduced into a 3.0 L container that is heated to 600°C. According to the information above, which of the following will occur as the system approaches equilibrium?

(A) More $H_2(g)$ will be produced because $Q > K_c$.
(B) More $I_2(g)$ will be produced because $Q < K_c$.
(C) More $HI(g)$ will be produced because $Q < K_c$.
(D) No change will occur because $Q = K_c$.

Reaction 1 : $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(l)$ $\qquad \Delta G° = -1010\ \text{kJ/mol}_{rxn}$

Reaction 2 : $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$ $\qquad \Delta G° = 70\ \text{kJ/mol}_{rxn}$

Reaction 3 : $4\ NO_2(g) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ HNO_3(aq)$ $\qquad \Delta G° = -170\ \text{kJ/mol}_{rxn}$

38. Based on the values of $\Delta G°$ for the three reactions represented above, what is the value of $\Delta G°$ for the reaction represented below?

$$4\ NH_3(g) + 8\ O_2(g) \rightarrow 4\ HNO_3(aq) + 4\ H_2O(l)$$

(A) $-1040\ \text{kJ/mol}_{rxn}$
(B) $-1110\ \text{kJ/mol}_{rxn}$
(C) $-1250\ \text{kJ/mol}_{rxn}$
(D) $-1320\ \text{kJ/mol}_{rxn}$

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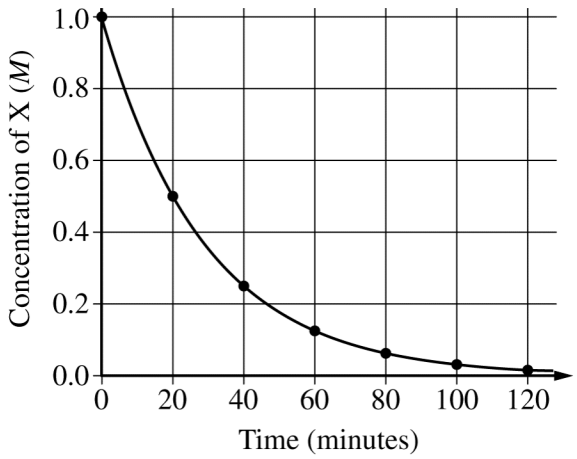
$$HCHO_2(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CHO_2^-(aq)$$

39. $HCHO_2(aq)$, a weak acid ($K_a = 2 \times 10^{-4}$), dissociates in water according to the equation above. Which of the following provides the best estimate of the pH of 0.5 M $HCHO_2(aq)$ and identifies the species at the highest concentration (excluding H_2O) in the solution?

	pH	Species at Highest Concentration
(A)	1	$H_3O^+(aq)$
(B)	1	$HCHO_2(aq)$
(C)	2	$H_3O^+(aq)$
(D)	2	$HCHO_2(aq)$

$$X \rightarrow \text{Products}$$

40. A student studied the kinetics of the reaction represented above by measuring the concentration of the reactant, X, over time. The data are plotted in the graph below.



Which of the following procedures will allow the student to determine the rate constant, k, for the reaction?

(A) Plot ln [X] versus time and determine the magnitude of the slope.

(B) Plot $\frac{1}{[X]}$ versus time and determine the magnitude of the slope.

(C) Run another trial of the experiment with a different initial concentration, plot the data on the same graph, and see where the curves intersect.

(D) Run another trial of the experiment at a different temperature, plot the data on the same graph, and see where the curves have the same slope.

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$CH_4(g) + Cl(g) \rightarrow CH_3(g) + HCl(g) \qquad \Delta H° = -14 \text{ kJ/mol}_{rxn}$

$NH_3(g) + Cl(g) \rightarrow NH_2(g) + HCl(g) \qquad \Delta H° = -36 \text{ kJ/mol}_{rxn}$

$H_2O(g) + Cl(g) \rightarrow OH(g) + HCl(g) \qquad \Delta H° = +40 \text{ kJ/mol}_{rxn}$

41. Based on the data above, what can be concluded regarding the strength of the C−H, N−H, and O−H bonds in the molecules shown?

(A) The C−H bond is the strongest.
(B) The N−H bond is the strongest.
(C) The O−H bond is the strongest.
(D) Nothing can be concluded without knowing the strength of the H−Cl bond.

Reaction	K_{eq}
$SO_2(g) + \frac{1}{2} O_2(g) \rightleftarrows SO_3(g)$	K_1
$2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g)$	K_2

42. Which of the following shows the relationship between K_1 and K_2 in the reactions represented above?

(A) $K_2 = (K_1)^2$

(B) $K_2 = \sqrt{K_1}$

(C) $K_2 = \frac{1}{(K_1)^2}$

(D) $K_2 = \frac{1}{K_1}$

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Questions 43-46 refer to the following information.

$$2\ NO_2(g) \rightleftarrows N_2O_4(g)$$

dark brown *colorless*

The dimerization of $NO_2(g)$, an exothermic process, is represented by the equation above.

43. Which of the following experimental techniques will allow the most accurate determination of the concentration of $NO_2(g)$ at equilibrium?

(A) Paper chromatography
(B) Gravimetric analysis
(C) Titration
(D) Spectrophotometry

44. The forward reaction is thermodynamically favored at which of the following temperatures?

(A) All temperatures
(B) Low temperatures only
(C) High temperatures only
(D) No temperature

45. A 0.0300 mol sample of $NO_2(g)$ is placed in a rigid 1.00 L reaction vessel and allowed to reach equilibrium at a certain temperature. What is the value of K_c at this temperature if 0.00500 mol of $N_2O_4(g)$ is present at equilibrium?

(A) 0.0800
(B) 0.250
(C) 4.00
(D) 12.5

46. A mixture of $NO_2(g)$ and $N_2O_4(g)$ is at equilibrium in a rigid reaction vessel. If the temperature of the mixture is decreased, then

(A) $[NO_2]$ will increase and the mixture will turn a darker brown
(B) $[N_2O_4]$ will increase and the mixture will turn a lighter brown
(C) $[N_2O_4]$ will decrease and the mixture will turn a lighter brown
(D) no change will be observed

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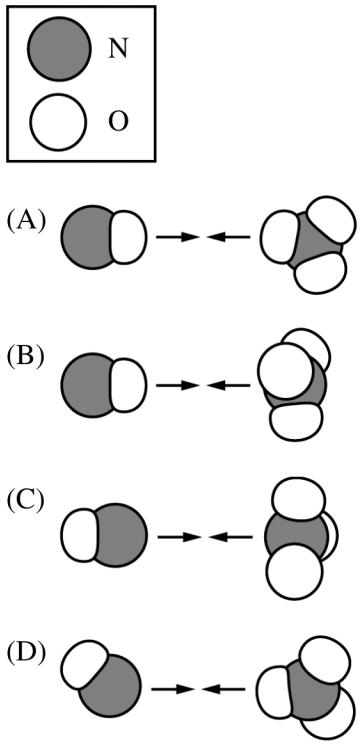
$$NO(g) + NO_3(g) \rightarrow 2\,NO_2(g)$$

47. The reaction between $NO(g)$ and $NO_3(g)$ is represented by the equation above. Which of the following orientations of collision between $NO(g)$ and $NO_3(g)$ is most likely to be effective?



$$N_2O(g) + CO(g) \rightarrow N_2(g) + CO_2(g)$$

48. The rate of the reaction represented above increases significantly in the presence of $Pd(s)$. Which of the following best explains this observation?

(A) Pd increases the activation energy of the reaction.
(B) Pd absorbs the heat produced in the reaction.
(C) One of the reactants binds on the surface of Pd, which introduces an alternative reaction pathway with a lower activation energy.
(D) One of the products binds on the surface of Pd, which increases the reaction rate by decreasing the concentration of products in the mixture.

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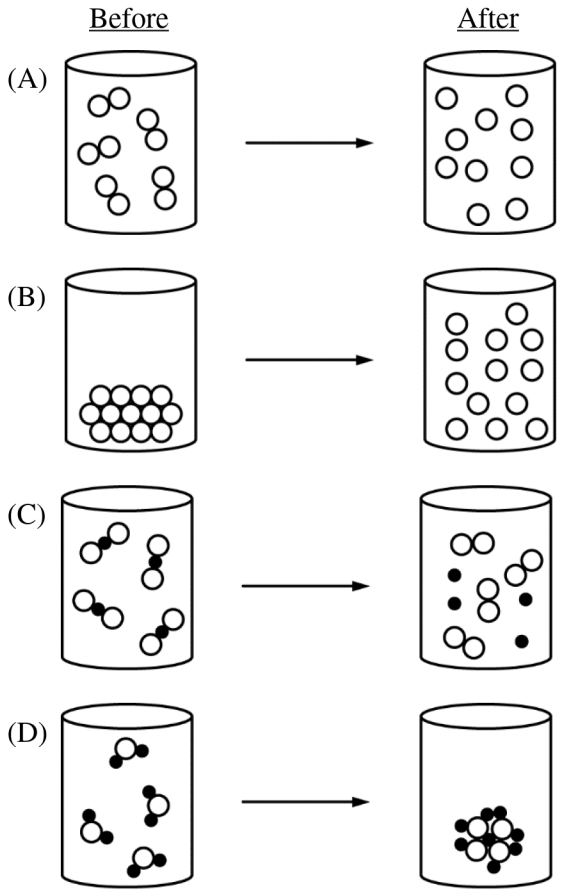
49. Which of the following particulate representations shows a process during which the entropy of the system decreases?



50. A 50.0 g sample of Fe at 100°C is added to 500.0 mL of water at 35°C in a perfectly insulated container. Which of the following statements is true?

(A) The temperature of the water will decrease.
(B) The temperature change of the Fe will have the same magnitude as the temperature change of the water.
(C) The heat energy lost by the Fe will be less than the heat energy gained by the water.
(D) The heat energy lost by the Fe will be equal to the heat energy gained by the water.

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CHEMISTRY

Section II

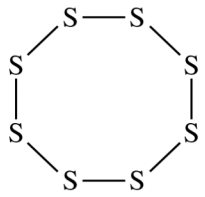
Time—1 hour and 45 minutes

7 Questions

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.



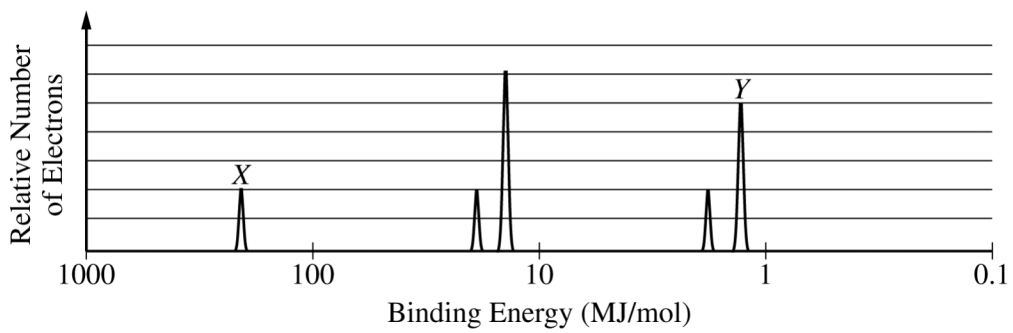
1. Elemental sulfur can exist as molecules with the formula Sg. The Sg molecule is represented by the incomplete Lewis diagram above.

   (a) The diagram of S_8 shows only bonding pairs of electrons. How many lone pairs of electrons does each S atom in the molecule have?

   (b) Based on your answer to part (a), determine the expected value of the S–S–S bond angles in the S_8 molecule.

   (c) Write the electron configuration for the S atom in its ground state.

   (d) The complete photoelectron spectrum for the element chlorine is represented below. Peak *X* in the spectrum corresponds to the binding energy of electrons in a certain orbital of chlorine atoms. The electrons in this orbital of chlorine have a binding energy of 273 MJ/mol, while the electrons in the same orbital of sulfur atoms have a binding energy of 239 MJ/mol.



   (i) Identify the orbital and explain the difference between the binding energies in terms of Coulombic forces.

   (ii) Peak *Y* corresponds to the electrons in certain orbitals of chlorine atoms. On the spectrum shown, carefully draw the peak that would correspond to the electrons in the same orbitals of sulfur atoms.

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$$3\ S_8 + 8\ OH^- \rightarrow 8\ S_3^- + 4\ HOOH$$

In an experiment, a student studies the kinetics of the reaction represented above and obtains the data shown in the following table.

Experiment	Initial $[S_8]$ (M)	Initial $[OH^-]$ (M)	Initial Reaction Rate (M/s)
Trial 1	0.100	0.0100	0.699
Trial 2	0.300	0.0100	2.10
Trial 3	0.300	?	4.19

(e) Use the data in the table to do the following.

(i) Determine the order of the reaction with respect to Ss. Justify your answer.

(ii) Determine the value of $[OH^-]$ that was used in trial 3, considering that the reaction is first order with respect to OH^-. Justify your answer.

The next day the student conducts trial 4 using the same concentrations of S_8 and OH^- as in trial 1, but the reaction occurs at a much slower rate than the reaction in trial 1. The student observes that the temperature in the lab is lower than it was the day before.

(f) Using particle-level reasoning, provide TWO explanations that help to account for the fact that the reaction rate is slower in trial 4.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

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2. Answer the following questions relating to HCl, CH_3Cl, and CH_3Br.

(a) $HCl(g)$ can be prepared by the reaction of concentrated $H_2SO_4(aq)$ with $NaCl(s)$, as represented by the following equation.

$$H_2SO_4(aq) + 2\ NaCl(s) \rightarrow 2\ HCl(g) + Na_2SO_4(aq)$$

(i) A student claims that the reaction is a redox reaction. Is the student correct? Justify your answer.

(ii) Calculate the mass, in grams, of $NaCl(s)$ needed to react with excess $H_2SO_4(aq)$ to produce 3.00 g of $HCl(g)$. Assume that the reaction goes to completion.

$HCl(g)$ can react with methanol vapor, $CH_3OH(g)$, to produce $CH_3Cl(g)$, as represented by the following equation.

$$CH_3OH(g) + HCl(g) \rightleftarrows CH_3Cl(g) + H_2O(g) \qquad K_p = 4.7 \times 10^3 \text{ at } 400 \text{ K}$$

(b) $CH_3OH(g)$ and $HCl(g)$ are combined in a 10.00 L sealed reaction vessel and allowed to reach equilibrium at 400 K. The initial partial pressure of $CH_3OH(g)$ in the vessel is 0.250 atm and that of $HCl(g)$ is 0.600 atm.

(i) Does the total pressure in the vessel increase, decrease, or remain the same as equilibrium is approached? Justify your answer in terms of the reaction stoichiometry.

(ii) Considering the value of K_p, calculate the final partial pressure of $HCl(g)$ after the system inside the vessel reaches equilibrium at 400 K.

(iii) The student claims that the final partial pressure of $CH_3OH(g)$ at equilibrium is very small but not exactly zero. Do you agree or disagree with the student's claim? Justify your answer.

(c) The table below shows some data for the compounds CH_3Cl and CH_3Br.

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)	$\Delta H^\circ_{vaporization}$ (kJ/mol)
CH_3Cl	50.5	1.87	249	18.9
CH_3Br	94.9	1.81	277	22.8

(i) Identify all the types of intermolecular forces that exist among molecules in $CH_3Cl(l)$.

(ii) In terms of intermolecular forces, explain why the boiling point of $CH_3Br(l)$ is greater than that of $CH_3Cl(l)$.

(d) A 2.00 mL sealed glass vial containing a 1.00 g sample of $CH_3Cl(l)$ is stored in a freezer at 233 K.

(i) Calculate the pressure in the vial at 298 K assuming that all the $CH_3Cl(l)$ vaporizes.

(ii) Explain why it would be unsafe to remove the vial from the freezer and leave it on a lab bench at 298 K.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

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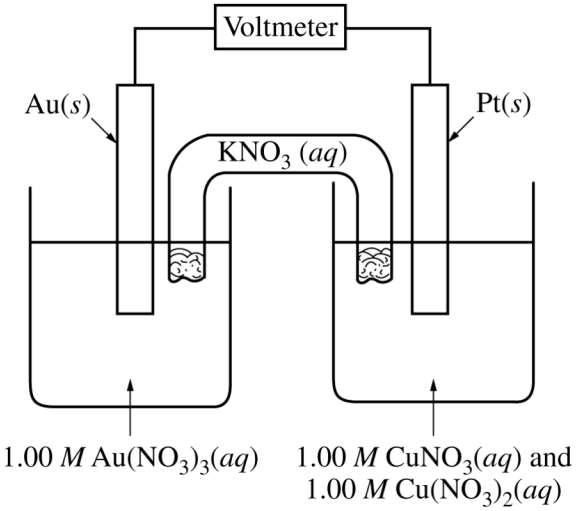
$$3\ Cu^{+}(aq) + Au^{3+}(aq) \rightarrow 3\ Cu^{2+}(aq) + Au(s)$$

3. A student studying the reaction represented above constructs a voltaic cell as shown in the diagram below. The cell contains an $Au(s)$ electrode in a beaker containing 1.00 M $Au(NO_3)_3(aq)$ and a $Pt(s)$ electrode in a beaker containing 1.00 M $CuNO_3(aq)$ and 1.00 M $Cu(NO_3)_2(aq)$.



The standard reduction potentials associated with the cell are given in the following table.

Half-reaction	$E°$ (V)
$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$	0.16
$Au^{3+}(aq) + 3\ e^{-} \rightarrow Au(s)$	1.50

(a) Calculate the value of the standard cell potential, $E°$.

(b) Does the mass of the $Pt(s)$ electrode increase, decrease, or remain the same as the cell operates? Justify your answer.

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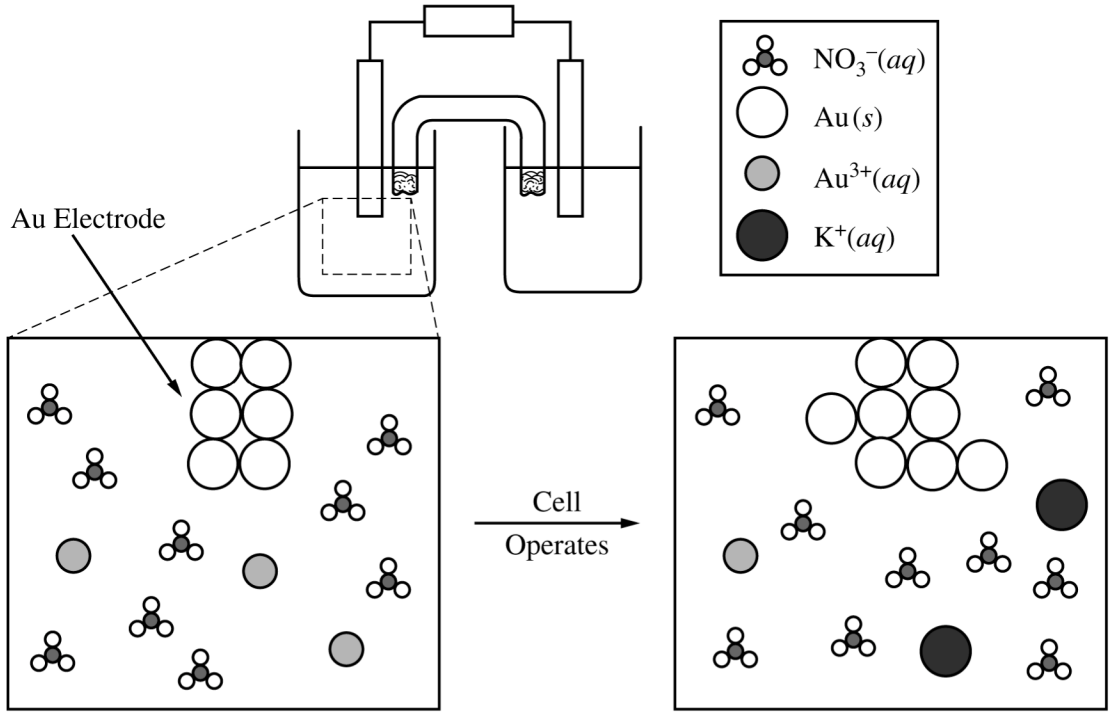
An expanded view of the Au half-cell before the reaction occurs is shown in box A below. An expanded view of the Au electrode after the cell operates for a period of time is shown in box B below.



(c) Assuming that the representation in box A is accurate, explain what is wrong with the stoichiometry represented in box B.

(d) After the cell has operated for 30.0 minutes, 0.185 g of Au(*s*) is deposited on the Au electrode.

(i) Calculate the number of moles of Au(s) deposited.

(ii) Calculate the average current that passed through the cell during the deposition of Au(s).

The student adds some NaCl(*s*) to the half-cell that contains $Cu^+(aq)$ and $Cu^{2+}(aq)$, and a precipitate forms.

(e) Based on the information in the following table, determine the identity of the precipitate. Justify your answer with a calculation.

Compound	Solubility (mol/L)	K_{sp}
CuCl	?	1.7×10^{-7}
$CuCl_2$	5.2	?

(f) Write the net ionic equation for the formation of the precipitate.

(g) The student predicts that the cell voltage will increase after the precipitate forms. Do you agree with the student's prediction? Justify your answer.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

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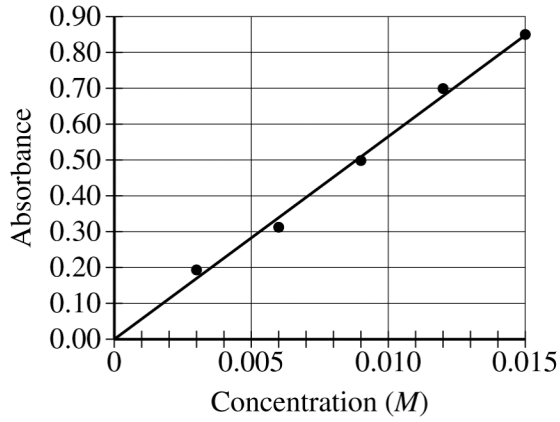
4. To spectrophotometrically determine the mass percent of cobalt in an ore containing cobalt and some inert materials, solutions with known $[Co^{2+}]$ are prepared and the absorbance of each of the solutions is measured at the wavelength of optimum absorbance. The data are used to create a calibration plot, shown below.



A 0.630 g sample of the ore is completely dissolved in concentrated $HNO_3(aq)$. The mixture is diluted with water to a final volume of 50.00 mL. Assume that all the cobalt in the ore sample is converted to $Co^{2+}(aq)$.

(a) What is the $[Co^{2+}]$ in the solution if the absorbance of a sample of the solution is 0.74 ?

(b) Calculate the number of moles of $Co^{2+}(aq)$ in the 50.00 mL solution.

(c) Calculate the mass percent of Co in the 0.630 g sample of the ore.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 4

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$$3\ Ag(s) + 4\ HNO_3(aq) \rightarrow 3\ AgNO_3(aq) + NO(g) + 2\ H_2O(l)$$

5. A student investigates the reaction between $Ag(s)$ and $HNO_3(aq)$ represented by the equation above.

   (a) Predict the sign of the entropy change, $\Delta S°$, for the reaction. Justify your answer.

   (b) Use the information in the table below to calculate the value of AHin, the standard enthalpy change for the reaction, in kJ/mol$_{rxn}$.

Substance	$HNO_3(aq)$	$AgNO_3(aq)$	$NO(g)$	$H_2O(l)$
Standard Heat of Formation, ΔH_f° (kJ/mol)	−207	−101	90.	−286

   (c) Based on your answers to parts (a) and (b), is the reaction more likely to be thermodynamically favorable at 25°C, or at 95°C? Justify your answer.

   (d) The student runs the reaction using a 3 to 4 mole ratio of $Ag(s)$ to $HNO_3(aq)$. Suggest a method the student can use to isolate solid $AgNO_3$ from the other products of the reaction.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 5

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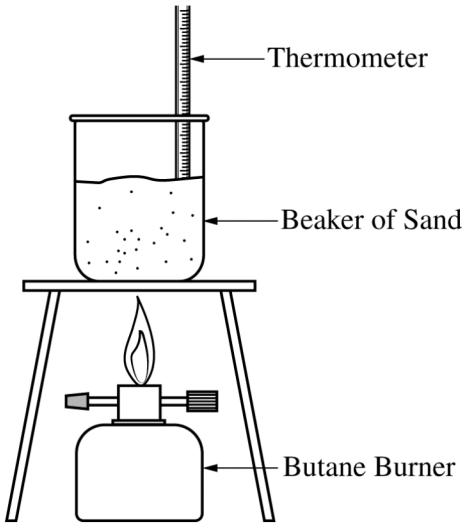
6. A student is asked to determine what mass of butane, $C_4H_{10}(g)$, needs to burn in order to raise the temperature of a 1650 g beaker of sand by 180.°C. The student is provided with the equipment shown below.



(a) Calculate the amount of heat energy needed to raise the temperature of the beaker of sand by 180.°C. Assume that all the heat energy from the burner is transferred to the beaker of sand and that the specific heat capacity of the beaker and sand together is 0.810 J/(g·°C).

The student runs the experiment and collects the data shown in the table below.

Mass of the beaker and sand	1650 g
Mass of butane burner before combustion	225.26 g
Mass of butane burner after combustion	218.20 g
Initial temperature of the beaker of sand	20.°C
Final temperature of the beaker of sand	200.°C

(b) Calculate the number of moles of butane that was used in the experiment. Report your answer to the appropriate number of significant figures.

The combustion of butane is represented by the equation below.

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 5\ H_2O(g) + 4\ CO_2(g) \qquad \Delta H^\circ_{rxn} = -2659\ \text{kJ/mol}_{rxn}$$

(c) Using the balanced equation for the combustion of butane and AHixn, determine the amount of heat energy produced by the combustion of butane in the experiment.

(d) The student claims that some of the heat energy produced by the combustion of butane was lost to the air surrounding the system. Do your answers to parts (a) and (c) support the student's claim? Explain.

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PAGE FOR ANSWERING QUESTION 6

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Solution X	100 mL of 0.10 *M* NaOH(*aq*) is mixed with 100 mL of 0.10 *M* HBr(*aq*)
Solution Y	100 mL of 0.10 *M* NaBr(*aq*) is mixed with 100 mL of 0.10 *M* HBr(*aq*)
Solution Z	100 mL of 0.10 *M* $HC_2H_3O_2(aq)$ is mixed with 100 mL of 0.10 *M* $NaC_2H_3O_2(aq)$

7. A student prepares three solutions, X, Y, and Z, as described in the table above. The values of K_a for the acidic species in the solutions are given in the table below.

Species	K_a
HBr(*aq*)	>>1 (very large)
$HC_2H_3O_2(aq)$	1.8×10^{-5}

(a) Using the information above, write the letters of the solutions in the boxes below to rank the solutions in order of increasing pH. Explain your reasoning for the ranking.

Lowest pH Highest pH

	<		<	

(b) Does the pH of solution Y increase, decrease, or remain the same when 100 mL of water is added? Justify your answer.

(c) The student adds 0.0010 mol of NaOH(*s*) to solution Y, and adds 0.0010 mol of NaOH(*s*) to solution Z. Assume that the volume of each solution does not change when the NaOH(*s*) is added. The pH of solution Y changes much more than the pH of solution Z changes. Explain this observation.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 7

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PERIODIC TABLE OF THE ELEMENTS

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

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

AP® CHEMISTRY EQUATIONS AND CONSTANTS

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

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

ATOMIC STRUCTURE

$E = h\nu$

$c = \lambda\nu$

E = energy
ν = frequency
λ = wavelength

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

EQUILIBRIUM

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

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

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

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

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

$= K_a \times K_b$

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

$14 = pH + pOH$

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

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

Equilibrium Constants

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

KINETICS

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

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

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

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

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

Molarity, M = moles of solute per liter of solution

$$A = abc$$

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

Gas constant, R = 8.314 J $\text{mol}^{-1}\,\text{K}^{-1}$
= 0.08206 L atm $\text{mol}^{-1}\,\text{K}^{-1}$
= 62.36 L torr $\text{mol}^{-1}\,\text{K}^{-1}$

1 atm = 760 mm Hg = 760 torr

STP = 273.15 K and 1.0 atm

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

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

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

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

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

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