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. In which of the following processes will ΔS° be negative?

   (A) $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$
   (B) $NaCl(s) \rightarrow NaCl(l)$
   (C) $CO_2(s) \rightarrow CO_2(g)$
   (D) $Cl_2(g) \rightarrow Cl_2(l)$

Solution
0.1 *M* $HC_2H_3O_2(aq)$
0.1 *M* $KI(aq)$
0.1 *M* $CH_3OH(aq)$

2. Of the three solutions listed in the table above, which one, if any, has the greatest electrical conductivity and why?

   (A) 0.1 *M* $HC_2H_3O_2(aq)$ because its molecules have the most atoms.
   (B) 0.1 *M* $KI(aq)$ because KI completely dissociates in water to produce ions.
   (C) 0.1 *M* $CH_3OH(aq)$ because its molecules can form hydrogen bonds.
   (D) All three solutions have the same electrical conductivity because the concentrations are the same.

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$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$$

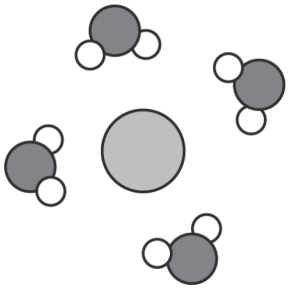
3. Hydrogen gas reacts with iodine gas at constant temperature in a sealed rigid container. The gases are allowed to reach equilibrium according to the equation above. Which of the following best describes what will happen to the reaction immediately after additional iodine gas is added to the system?

   (A) The rates of both the forward and reverse reactions decrease.
   (B) The rates of both the forward and reverse reactions do not change.
   (C) The rate of the forward reaction becomes greater than the rate of the reverse reaction.
   (D) The rate of the forward reaction becomes less than the rate of the reverse reaction.

	Ionization Energy (kJ/mol)
First	578
Second	1,817
Third	2,745
Fourth	11,577
Fifth	14,842

4. The first five ionization energies of an unknown element are listed in the table above. Which of the following statements correctly identifies the element and cites the evidence supporting the identification?

   (A) Na, because of the large difference between the first and the second ionization energies
   (B) Al, because of the large difference between the third and fourth ionization energies
   (C) Si, because the fifth ionization energy has the greatest value
   (D) P, because a neutral atom of P has five valence electrons



5. The diagram above represents a particle in aqueous solution. Which of the following statements about the particle is correct?

   (A) The particle must be a cation because the negative end of each water molecule is pointed toward it.
   (B) The particle must be an anion because the positive end of each water molecule is pointed toward it.
   (C) The charge of the particle cannot be determined because water molecules have no net charge.
   (D) The charge of the particle cannot be determined because the water molecules are arranged symmetrically and their partial charges cancel.

Compound	Formula	Boiling Point (°C)	Density (g/mL)
Hexane	C_6H_{14}	69	0.66
Octane	C_8H_{18}	126	0.70

6. A student obtains a mixture of the liquids hexane and octane, which are miscible in all proportions. Which of the following techniques would be best for separating the two components of the mixture, and why?

   (A) Filtration, because the different densities of the liquids would allow one to pass through the filter paper while the other would not.
   (B) Paper chromatography, because the liquids would move along the stationary phase at different rates owing to the difference in polarity of their molecules.
   (C) Column chromatography, because the higher molar mass of octane would cause it to move down the column faster than hexane.
   (D) Distillation, because the liquids would boil at different temperatures owing to the difference in strength of their intermolecular forces.

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$$Ge(g) + 2\,Cl_2(g) \rightleftarrows GeCl_4(g)$$

7. The value of the equilibrium constant for the reaction represented above is 1×10^{10}. What is the value of the equilibrium constant for the following reaction?

$$2\,GeCl_4(g) \rightleftarrows 2\,Ge(g) + 4\,Cl_2(g)$$

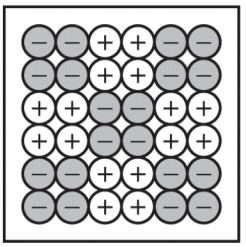
(A) 1×10^{-20}
(B) 1×10^{-10}
(C) 1×10^{10}
(D) 1×10^{20}

8. To catalyze a biochemical reaction, an enzyme typically

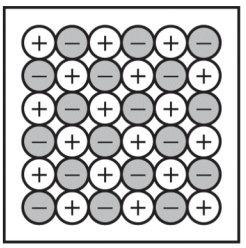
(A) drives the reaction to completion by consuming byproducts of the reaction
(B) binds temporarily to reactant molecules to lower the activation energy of the reaction
(C) dissociates into additional reactant molecules, thereby increasing the reaction rate
(D) decomposes and releases energy to increase the number of successful collisions between reactant molecules

9. Of the following diagrams, which best represents the structure of solid KF ?

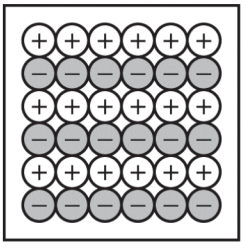
(A)



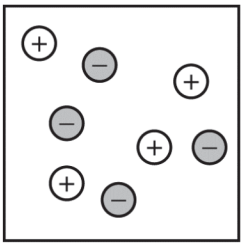
(B)



(C)



(D)



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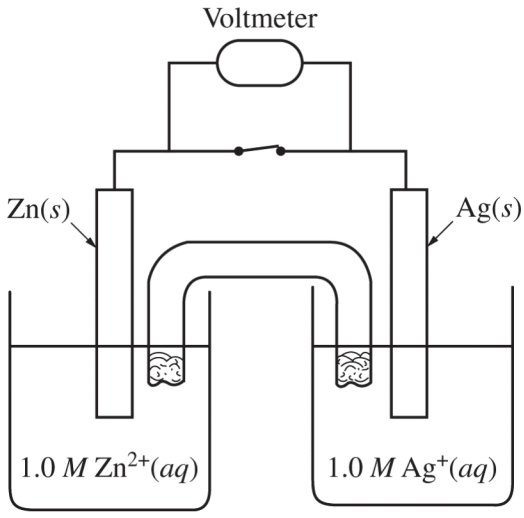
Questions 10-11 refer to the following information.



Standard reduction potentials for the half-reactions associated with the electrochemical cell shown above are given in the table below.

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

10. Which of the following is the net ionic equation for the overall reaction that occurs as the cell operates?

(A) $Ag(s) + Zn^{2+}(aq) \rightarrow Ag^{2+}(aq) + Zn(s)$
(B) $Ag^+(aq) + Zn^{2+}(aq) + 3\ e^- \rightarrow AgZn(s)$
(C) $Ag^+(aq) + Zn(s) \rightarrow Ag(s) + Zn^{2+}(aq) + e^-$
(D) $2\ Ag^+(aq) + Zn(s) \rightarrow 2\ Ag(s) + Zn^{2+}(aq)$

11. What is the value of E° for the cell?

(A) 0.04 V
(B) 0.84 V
(C) 1.56 V
(D) 2.36 V

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$$CO_2(g) + 2\ LiOH(s) \rightarrow Li_2CO_3(aq) + H_2O(l)$$

12. In a one-person spacecraft, an astronaut exhales 880 g of $CO_2(g)$ (molar mass 44 g/mol) per day. To prevent the buildup of $CO_2(g)$ in the spacecraft, a device containing $LiOH(s)$ is used to remove the $CO_2(g)$, as represented by the equation above. What mass of $LiOH(s)$ (molar mass 24 g/mol) is needed to react with all of the $CO_2(g)$ produced by an astronaut in one day?

(A) 40. g
(B) 240 g
(C) 480 g
(D) 960 g

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Time (s)	$[NO_2]$ (mol/L)	ln $[NO_2]$	$\frac{1}{[NO_2]}$ (L/mol)
0	0.500	–0.693	2.00
100	0.364	–1.01	2.75
200	0.286	–1.25	3.50
300	0.235	–1.45	4.25

13. The data from a study of the decomposition of $NO_2(g)$ to form $NO(g)$ and $O_2(g)$ are given in the table above. Which of the following rate laws is consistent with the data?

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

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

(C) Rate = $k\,\frac{1}{[NO_2]}$

(D) Rate = $k\,\frac{1}{[NO_2]^2}$

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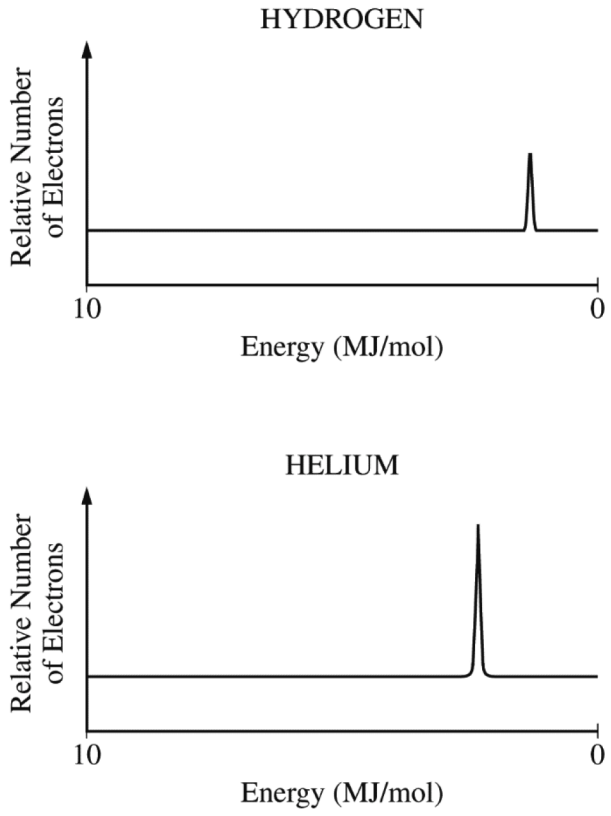

14. The photoelectron spectra for H and He are represented above. Which of the following statements best accounts for the fact that the peak on the He spectrum is farther to the left and higher than the peak on the H spectrum?

(A) He has an additional valence electron in a higher energy level than the valence electron in H.
(B) He has a greater nuclear charge than H and an additional electron in the same energy level.
(C) He has a completely filled valence shell in which the electrons are a greater distance from the nucleus than the distance between the H nucleus and its electron.
(D) It takes longer for the electrons in He to be removed due to the higher nuclear mass of He.

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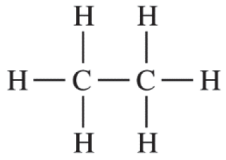
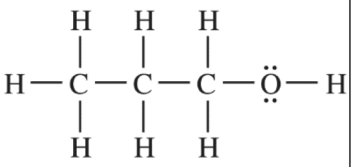
Questions 15-19 are based on the information in the table below.

Compound	Molar Mass	Balanced Equation for the Combustion of One Mole of the Compound	ΔH°_{comb} (kJ/mol$_{rxn}$)
 Ethane	30. g/mol	$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l)$	−1560
 Propanol	60. g/mol	$C_3H_8O(l) + \frac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$	−2020
Unknown	?	$? + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 4\,H_2O(l)$	−2240

15. Which of the following is the molecular formula of the unknown compound?

(A) C_4H_8

(B) C_4H_8O

(C) $C_4H_4O_2$

(D) $C_4H_8O_2$

16. Which of the following best explains why the combustion reactions represented in the table are exothermic?

(A) The number of bonds in the reactant molecules is greater than the number of bonds in the product molecules.

(B) The number of bonds in the reactant molecules is less than the number of bonds in the product molecules.

(C) The energy required to break the bonds in the reactants is greater than the energy released in forming the bonds in the products.

(D) The energy required to break the bonds in the reactants is less than the energy released in forming the bonds in the products.

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17. Based on the structural formulas, which of the following identifies the compound that is more soluble in water and best helps to explain why?

(A) Ethane, because the electron clouds of its molecules are more polarizable than those of propanol.

(B) Ethane, because its molecules can fit into the spaces between water molecules more easily than those of propanol can.

(C) Propanol, because its molecules have a greater mass than the molecules of ethane have.

(D) Propanol, because its molecules can form hydrogen bonds with water molecules but those of ethane cannot.

18. In an experiment, 30.0 g of ethane and 30.0 g of propanol are placed in separate reaction vessels. Each compound undergoes complete combustion with excess $O_2(g)$. Which of the following best compares the quantity of heat released in each combustion reaction?

(A) $q_{ethane} < q_{propanol}$

(B) $q_{ethane} = q_{propanol}$

(C) $q_{ethane} > q_{propanol}$

(D) The quantities of heat released in the combustions of ethane and propanol cannot be compared without knowing the specific heat capacity of the compounds.

19. A sealed 10.0 L flask at 400 K contains equimolar amounts of ethane and propanol in gaseous form. Which of the following statements concerning the average molecular speed of ethane and propanol is true?

(A) The average molecular speed of ethane is less than the average molecular speed of propanol.

(B) The average molecular speed of ethane is greater than the average molecular speed of propanol.

(C) The average molecular speed of ethane is equal to the average molecular speed of propanol.

(D) The average molecular speeds of ethane and propanol cannot be compared without knowing the total pressure of the gas mixture.

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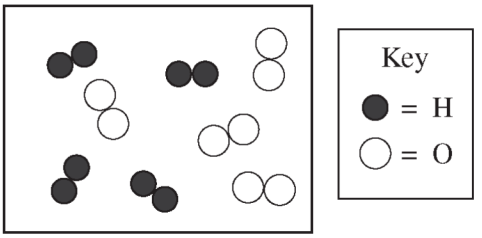
20. As a sample of $KNO_3(s)$ is stirred into water at 25°C, the compound dissolves endothermically. Which of the following best helps to explain why the process is thermodynamically favorable at 25°C?

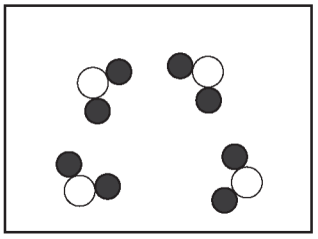
(A) All endothermic processes are thermodynamically favorable.
(B) Stirring the solution during dissolution adds the energy needed to drive an endothermic process.
(C) Dissolving the salt decreases the enthalpy of the system.
(D) Dissolving the salt increases the entropy of the system.

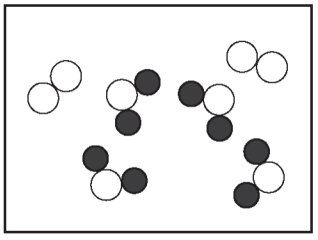
21. A solution is prepared by mixing equal volumes of 0.20 *M* $HC_2H_3O_2$ and 0.40 *M* $NaC_2H_3O_2$. Which of the following correctly describes what occurs if a small amount of HCl(*aq*) or NaOH(*aq*) is added?

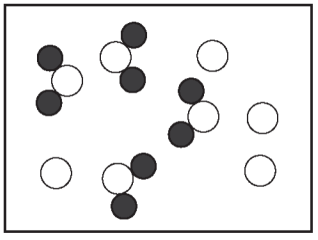
(A) If HCl(*aq*) is added, the pH will increase only slightly because the Cl^- ions will react with $C_2H_3O_2^-$ ions.
(B) If HCl(*aq*) is added, the pH will decrease only slightly because the Ht ions will react with $C_2H_3O_2^-$ ions.
(C) If NaOH(*aq*) is added, the pH will increase only slightly because the OH^- ions will react with $C_2H_3O_2^-$ ions.
(D) If NaOH(*aq*) is added, the pH will decrease only slightly because the OH^- ions will react with $HC_2H_3O_2$ molecules.

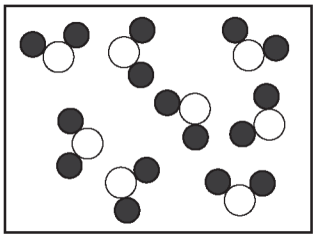


22. A mixture of $H_2(g)$ and $O_2(g)$ is placed in a container as represented above. The $H_2(g)$ and $O_2(g)$ react to form $H_2O(g)$. Which of the following best represents the container after the reaction has gone to completion?

(A)


(B)


(C)


(D)


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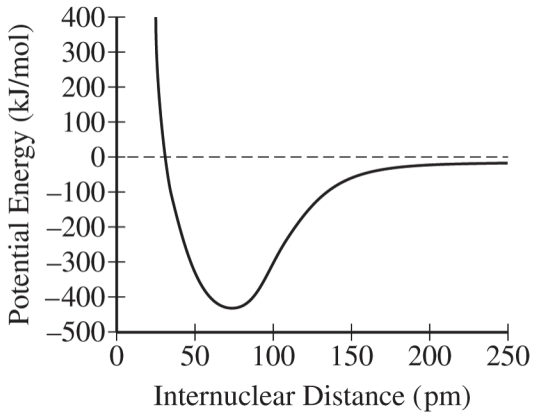
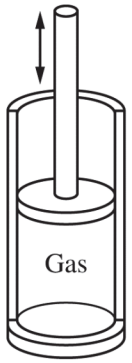
23. After a certain pesticide compound is applied to crops, its decomposition is a first-order reaction with a half-life of 56 days. What is the rate constant, k, for the decomposition reaction?

(A) $0.012\ \text{day}^{-1}$
(B) $0.018\ \text{day}^{-1}$
(C) $56\ \text{day}^{-1}$
(D) $81\ \text{day}^{-1}$



24. Which of the following can be inferred from the diagram above that shows the dependence of potential energy on the internuclear distance between two atoms?

(A) The atoms form a bond with a bond length of 25 pm.
(B) The atoms form a bond with a bond length of 75 pm.
(C) The net force between the atoms is attractive at 25 pm.
(D) The net force between the atoms is attractive at 75 pm.



25. A mixture of two gases, 0.01 mol of $C_4H_{10}(g)$ and 0.065 mol of $O_2(g)$, is pumped into a cylinder with a movable piston, as shown above. The mixture, originally at 200°C and 1.0 atm, is sparked and the reaction represented below occurs.

$$2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(g)$$

Which of the following is true after the product gases return to the original temperature and pressure, and why will the change occur? (Assume all gases behave ideally.)

(A) The piston will be higher than its original position, because the cylinder will contain a greater number of gas molecules.
(B) The position of the piston will be unchanged, because the total mass of the gases in the cylinder does not change.
(C) The position of the piston will be unchanged, because the temperature and pressure of the contents of the cylinder remain the same.
(D) The piston will be lower than its original position, because the product molecules are smaller than the reactant molecules.

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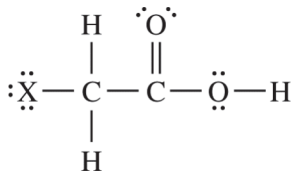
Questions 26-28 are based on the following information.



The structure of haloacetic acids, XCH_2COOH (where X is either F, Cl, Br, or I), is shown above. The dissociation constants and molar masses of four haloacetic acids are listed in the table below.

Acid	pK_a	K_a	Molar Mass (g/mol)
Fluoroacetic acid	2.59	2.57×10^{-3}	78.0
Chloroacetic acid	2.87	1.35×10^{-3}	94.5
Bromoacetic acid	2.90	1.26×10^{-3}	138.9
Iodoacetic acid	3.18	6.61×10^{-4}	185.9

26. Which compound, chloroacetic acid or iodoacetic acid, most likely has the lower boiling point, and why?

(A) Chloroacetic acid, because the London dispersion forces among its molecules are weaker.

(B) Chloroacetic acid, because the dipole-dipole forces among its molecules are weaker.

(C) Iodoacetic acid, because the London dispersion forces among its molecules are stronger.

(D) Iodoacetic acid, because the dipole-dipole forces among its molecules are stronger.

27. An aqueous solution contains small but equal concentrations of both chloroacetic and fluoroacetic acids. Which statement comparing the percent ionizations of the two acids in the solution is true?

(A) The percent ionization of chloroacetic acid is greater than that of fluoroacetic acid.

(B) The percent ionization of chloroacetic acid is less than that of fluoroacetic acid.

(C) The percent ionizations cannot be compared without knowing the concentrations of the two acids.

(D) The percent ionizations cannot be compared without knowing the pH of the solution.

28. A student titrates 10.0 mL samples of 1.0 *M* solutions of each of the haloacetic acids with a standard solution of NaOH. Which of the following statements correctly predicts the volume of NaOH(*aq*) needed to reach the equivalence point?

(A) Fluoroacetic acid will need the smallest volume of NaOH(*aq*) to reach the equivalence point.

(B) Iodoacetic acid will need the smallest volume of NaOH(*aq*) to reach the equivalence point.

(C) All of the acids will need the same volume of NaOH(*aq*) to reach the equivalence point.

(D) All of the haloacetic acids are weak; therefore none will reach an equivalence point.

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29. The value of K_w at 40°C is 3.0×10^{-14}. What is the pH of pure water at 40°C?

(A) 3.0
(B) 6.8
(C) 7.0
(D) 7.2

30. A 1.0 mol sample of He(g) at 25°C is mixed with a 1.0 mol sample of Xe(g) at 50°C. Which of the following correctly predicts the changes in average kinetic energy and the average speed of the Xe(g) atoms that will occur as the mixture approaches thermal equilibrium?

	Average Kinetic Energy of Xe Atoms	Average Speed of Xe Atoms
(A)	Will increase	Will increase
(B)	Will increase	Will decrease
(C)	Will decrease	Will increase
(D)	Will decrease	Will decrease

31. Which of the following best helps to explain why Na(s) is more reactive with water than Mg(s) is?

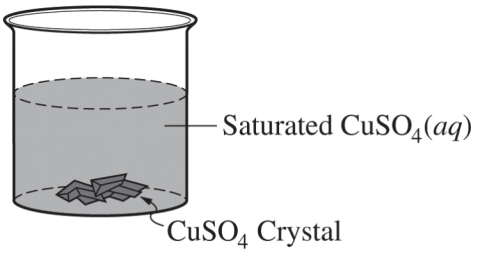
(A) Na(s) is softer than Mg(s).
(B) The atomic mass of Na is less than that of Mg.
(C) The Na^+ ion has weaker Coulombic attraction to an anion than the Mg^{2+} ion has.
(D) The first ionization energy of Na is less than that of Mg.

32. At 25°C, enough distilled water is added to a 30.0 mL sample of $HNO_3(aq)$ with a pH of 4.20 so that the final pH of the diluted solution is 5.20. The volume of distilled water added to the original solution is closest to

(A) 30.0 mL
(B) 60.0 mL
(C) 270. mL
(D) 300. mL

33. A student observes that the equilibrium constant for a reaction is greater than 1.0 at temperatures below 500 K but less than 1.0 at temperatures above 500 K. What can the student conclude about the values of $\Delta H°$ and $\Delta S°$ for the reaction? (Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.)

(A) $\Delta H° > 0$ and $\Delta S° > 0$
(B) $\Delta H° > 0$ and $\Delta S° < 0$
(C) $\Delta H° < 0$ and $\Delta S° > 0$
(D) $\Delta H° < 0$ and $\Delta S° < 0$



34. The saturated $CuSO_4(aq)$ shown above is left uncovered on a lab bench at a constant temperature. As the solution evaporates, 1.0 mL samples of the solution are removed every three days and the $[SO_4^{2-}]$ in the samples is measured. It is observed that the $[SO_4^{2-}]$ in the solution did not change over time. Which of the following best helps to explain the observation?

(A) As the solution evaporates, $Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$ leave the beaker along with the water molecules.
(B) As the solution evaporates, the dissolution of $CuSO_4(s)$ in the beaker decreases.
(C) The evaporation of water is endothermic, so more $CuSO_4(s)$ dissolves exothermically in the solution, which increases the $[SO_4^{2-}]$.
(D) As water evaporates, more $CuSO_4(s)$ precipitates out of the solution in the beaker.

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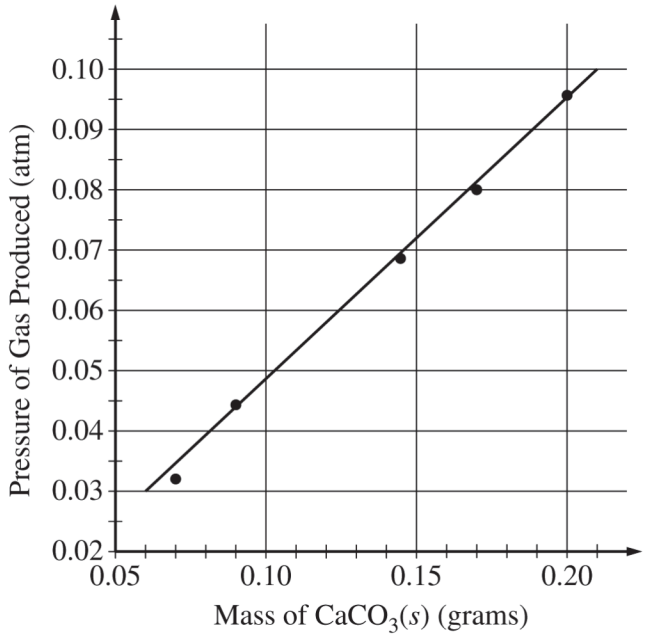
Questions 35-38 refer to the following information.

An experiment is performed to measure the mass percent of $CaCO_3(s)$ in eggshells. Five different samples of $CaCO_3(s)$ of known mass react with an excess of 2.0 M HCl(aq) in identical sealed, rigid reaction vessels. The pressure of the gas produced is measured with a pressure gauge attached to the reaction vessel. Since the reaction is exothermic, the reaction system is cooled to its original temperature before the pressure is recorded. The experimental data are used to create the calibration line below.



The experiment is repeated with an eggshell sample, and the experimental data are recorded in the table below.

Mass of eggshell sample	0.200 g
Pressure prior to reaction	0.800 atm
Pressure at completion of reaction	0.870 atm

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35. Which of the following equations best represents the species that react and the species that are produced when $CaCO_3(s)$ and $HCl(aq)$ are combined?

(A) $2\ H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) + H_2(g)$

(B) $2\ H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$

(C) $2\ H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq) + CO(g)$

(D) $2\ HCl(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g) + 2\ Cl^-(aq)$

36. The mass percent of $CaCO_3(s)$ in the eggshell sample is closest to

(A) 30%
(B) 45%
(C) 60%
(D) 75%

37. Another sample of eggshell reacts completely with 4.0 mL of an $HCl(aq)$ solution of unknown concentration. If the reaction produced 0.095 atm of gas, the concentration of the $HCl(aq)$ solution was at least

(A) 0.0020 *M*
(B) 0.050 *M*
(C) 0.50 *M*
(D) 1.0 *M*

38. Which of the following modifications will increase the rate of the reaction the most?

(A) Using 2.0 *M* $CH_3COOH(aq)$ instead of 2.0 *M* $HCl(aq)$
(B) Cooling the $HCl(aq)$ to a lower temperature than it was in the original experiment
(C) Reducing the volume of the reaction vessel
(D) Using eggshells that are more finely powdered than those used in the original experiment

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39. Samples of $NaF(s)$ and $NH_4Cl(s)$ are dissolved in separate beakers that each contain 100 mL of water. One of the salts produces a slightly acidic solution. Which of the following equations best represents the formation of the slightly acidic solution?

(A) $Na^+(aq) + 2\ H_2O(l) \rightleftarrows NaOH(aq) + H_3O^+(aq)$

(B) $F^-(aq) + H_2O(l) \rightleftarrows HF(aq) + OH^-(aq)$

(C) $NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$

(D) $Cl^-(aq) + H_2O(l) \rightleftarrows HCl(aq) + OH^-(aq)$

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$$\text{C(diamond)} \rightarrow \text{C(graphite)} \qquad \Delta G^\circ = -2.9 \text{ kJ/mol}_{rxn}$$

40. Which of the following best explains why the reaction represented above is not observed to occur at room temperature?

(A) The rate of the reaction is extremely slow because of the relatively small value of ΔG° for the reaction.

(B) The entropy of the system decreases because the carbon atoms in graphite are less ordered than those in diamond.

(C) The reaction has an extremely large activation energy due to strong three-dimensional bonding among carbon atoms in diamond.

(D) The reaction does not occur because it is not thermodynamically favorable.

$$C_9H_8O_4(aq) + NaOH(aq) \rightleftarrows C_9H_7O_4^-(aq) + Na^+(aq) + H_2O(l)$$

41. The reaction represented above occurs when 2.00×10^{-4} mol of pure acetylsalicylic acid, $C_9H_8O_4$, is completely dissolved in 15.00 mL of water in a flask and titrated to the equivalence point with 0.100 *M* NaOH(*aq*). Which of the following statements about the titration is true at the equivalence point?

(A) $[C_9H_8O_4]$ is greater than $[C_9H_7O_4^-]$.

(B) $[C_9H_8O_4]$ is less than $[C_9H_7O_4^-]$.

(C) $[C_9H_8O_4]$ is equal to $[C_9H_7O_4^-]$.

(D) The relationship between $[C_9H_8O_4]$ and $[C_9H_7O_4^-]$ cannot be determined without additional information.

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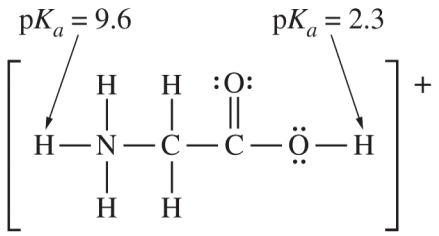
Questions 42-44 refer to the following.



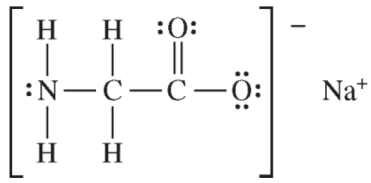
The structural formula of the glycinium cation is shown above. Arrows indicate the pK_a values for the labile protons in the molecule.

42. What is the approximate H–O–C bond angle in the glycinium cation?

(A) 180°
(B) 120°
(C) 105°
(D) 90°

43. Which of the following is true about the geometry of the glycinium cation?

(A) The leftmost C atom and all the atoms directly bonded to it lie in the same plane.
(B) Both C atoms and both O atoms lie in the same plane.
(C) The N–C–C bond angle is 180°.
(D) The geometry around the N atom is planar.



44. Which of the following statements is true about sodium glycinate, represented above?

(A) It is an ionic solid at room temperature.
(B) It is not soluble in water.
(C) It evaporates easily because of the lack of hydrogen bonding.
(D) It dissolves in water to form an acidic solution.

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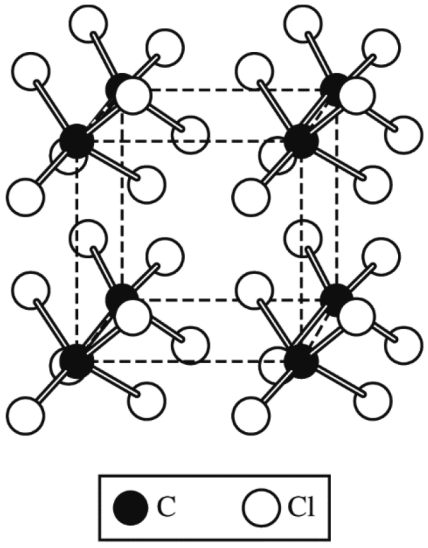

45. Solid carbon tetrachloride, $CCl_4(s)$, is represented by the diagram above. The attractions between the CCl molecules that hold the molecules together in the solid state are best identified as

(A) polar covalent bonds
(B) nonpolar covalent bonds
(C) intermolecular attractions resulting from temporary dipoles
(D) intermolecular attractions resulting from permanent dipoles

46. Which of the following is a list of the minimum amount of data needed for determining the molar enthalpy of solution of $KCl(s)$ in pure $H_2O(l)$? (Assume that the $KCl(aq)$ has the same specific heat capacity as pure water and that the initial temperatures of the $KCl(s)$ and the water are the same.)

(A) Mass of $KCl(s)$, initial temperature of the water, and final temperature of the solution
(B) Mass of H_2O, initial temperature of the water, and final temperature of the solution
(C) Mass of $KCl(s)$, mass of H_2O, initial temperature of the water, and final temperature of the solution
(D) Mass of $KCl(s)$, mass of H_2O, initial temperature of the water, final temperature of the solution, and atmospheric pressure

$$X_2(g) + Y_2(g) \rightleftarrows 2\,XY(g) \qquad K_c = 3.0$$

47. A mixture of $X_2(g)$, $Y_2(g)$, and $XY(g)$ is placed in a previously evacuated, rigid container and allowed to reach equilibrium at a constant temperature, as shown above. Which of the following sets of initial concentrations would lead to the formation of more product as the system moves toward equilibrium?

	$[X_2]_{initial}$	$[Y_2]_{initial}$	$[XY]_{initial}$
(A)	0.40 *M*	0.40 *M*	0.20 *M*
(B)	0.30 *M*	0.30 *M*	0.90 *M*
(C)	0.15 *M*	0.15 *M*	0.30 *M*
(D)	0.10 *M*	0.10 *M*	0.20 *M*

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cis-isomer *trans*-isomer

48. The structural formulas for two isomers of 1,2-dichloroethene are shown above. Which of the two liquids has the higher equilibrium vapor pressure at 20°C, and why?

(A) The *cis*-isomer, because it has dipole-dipole interactions, whereas the *trans*-isomer has only London dispersion forces

(B) The cis-isomer, because it has only London dispersion forces, whereas the *trans*-isomer also has dipole-dipole interactions

(C) The trans-isomer, because it has dipole-dipole interactions, whereas the *cis*-isomer has only London dispersion forces

(D) The *trans*-isomer, because it has only London dispersion forces, whereas the *cis*-isomer also has dipole-dipole interactions

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$$CaF_2(s) \rightleftarrows Ca^{2+}(aq) + 2\ F^-(aq) \qquad K_{sp} = 4.0 \times 10^{-11}$$

49. The concentration of $F^-(aq)$ in drinking water that is considered to be ideal for promoting dental health is $4.0 \times 10^{-5}\ M$. Based on the information above, the maximum concentration of $Ca^{2+}(aq)$ that can be present in drinking water without lowering the concentration of $F^-(aq)$ below the ideal level is closest to

(A) $0.25\ M$
(B) $0.025\ M$
(C) $1.6 \times 10^{-6}\ M$
(D) $1.6 \times 10^{-15}\ M$

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$$2\ FeO(s) \rightleftarrows 2\ Fe(s) + O_2(g) \qquad K_{eq} = 1 \times 10^{-6} \text{ at } 1000\ K$$

$$CO_2(g) \rightleftarrows C(s) + O_2(g) \qquad K_{eq} = 1 \times 10^{-32} \text{ at } 1000\ K$$

50. The formation of $Fe(s)$ and $O_2(g)$ from $FeO(s)$ is not thermodynamically favorable at room temperature. In an effort to make the process favorable, $C(s)$ is added to the $FeO(s)$ at elevated temperatures. Based on the information above, which of the following gives the value of K_{eq} and the sign of $\Delta G°$ for the reaction represented by the equation below at 1000 K?

$$2\ FeO(s) + C(s) \rightleftarrows 2\ Fe(s) + CO_2(g)$$

	K_{eq}	$\Delta G°$
(A)	1×10^{-38}	Positive
(B)	1×10^{-38}	Negative
(C)	1×10^{26}	Positive
(D)	1×10^{26}	Negative

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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.

$$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g) \qquad \Delta H^\circ_{comb} = -1270\ \text{kJ/mol}_{rxn}$$

1. Ethanol, C_2H_5OH, will combust in air according to the equation above.

   (a) Is $O_2(g)$ oxidized in the reaction, or is it reduced? Justify your answer in terms of oxidation numbers.

   (b) When a sample of C_2H_5OH was combusted, the volume of $CO_2(g)$ produced was 18.0 L when measured at 21.7°C and 1.03 atm. Determine the number of moles of $CO_2(g)$ that was produced.

   (c) Determine the volume of $C_2H_5OH(l)$, in mL, that was combusted to produce the volume of $CO_2(g)$ collected in part (b). (The density of $C_2H_5OH(l)$ is 0.79 g/mL.)

   (d) Determine the amount of heat, in kJ, that is released by the combustion reaction.

   The combustion reaction occurred in a closed room containing 5.56×10^4 g of air originally at 21.7°C. Assume that all of the heat produced by the reaction was absorbed by the air (specific heat = 1.005 J/(g °C)) in the room.

   (e) Determine the final temperature of the air in the room after the combustion.

   (f) The boiling points of ethanol and dimethyl ether are provided in the following table. Identify the intermolecular force that is most responsible for the difference in boiling point. In terms of this force, explain why the boiling point of ethanol is higher than that of dimethyl ether.

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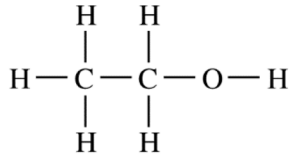
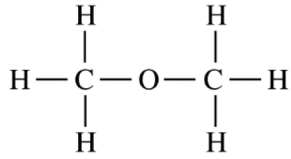
Compound	Structural Formula	Boiling Point (°C)
Ethanol		78
Dimethyl ether		–24

One method of producing ethanol is by the reaction of ethene and water, as represented below.

$$C_2H_4(g) + H_2O(g) \rightleftarrows C_2H_5OH(g) \qquad \Delta H^\circ = -45 \text{ kJ/mol}_{rxn}$$

(g) A chemist wants to run the reaction and maximize the amount of $C_2H_5OH(g)$ produced. Identify <u>two</u> ways the chemist could change the reaction conditions (other than adding or removing any chemical species) to favor the formation of more product. Justify your answer.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

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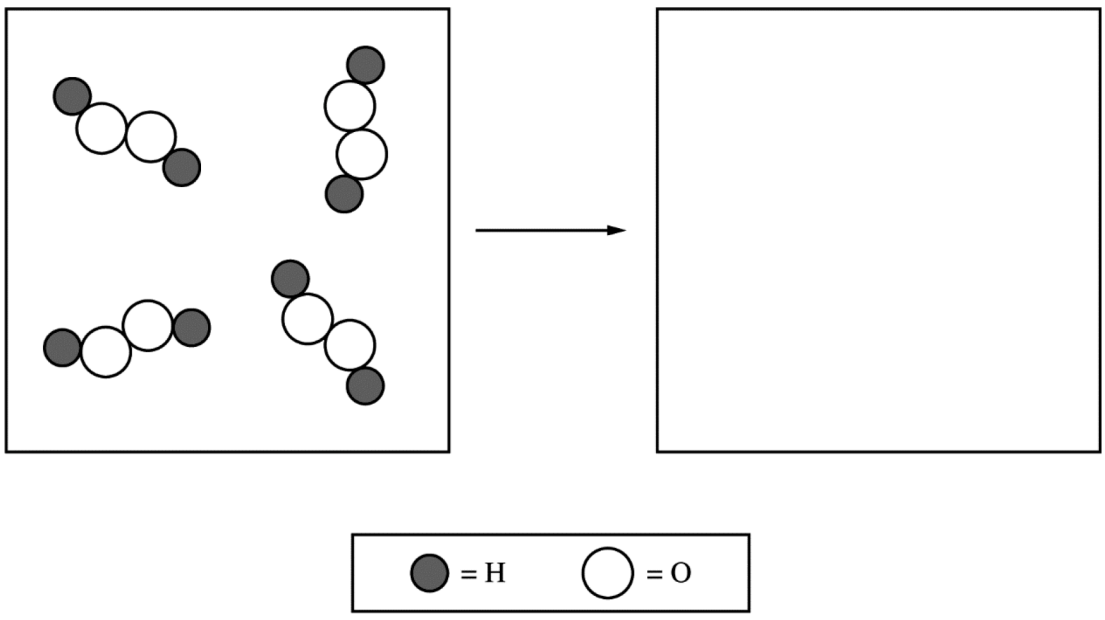
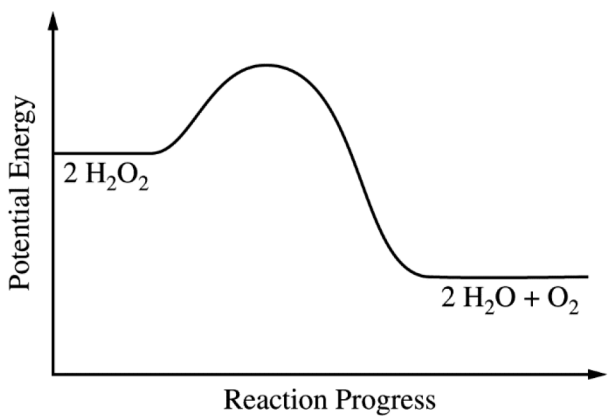
$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

2. Hydrogen peroxide, H_2O_2, decomposes according to the equation above. This reaction is thermodynamically favorable at room temperature.

   (a) A particulate representation of the reactants is shown below in the box on the left. In the box below on the right, draw the particulate representation of all the molecules that would be produced from these four reactant molecules.



   (b) Shown below is a potential energy diagram for the uncatalyzed decomposition of $H_2O_2(aq)$.



   (i) According to the diagram, is the decomposition reaction exothermic or endothermic? Justify your answer.

   (ii) Manganese dioxide, $MnO_2(s)$, is an insoluble substance that acts as a catalyst for the decomposition reaction. On the diagram above, draw a curve to represent the reaction as it occurs in the presence of $MnO_2(s)$.

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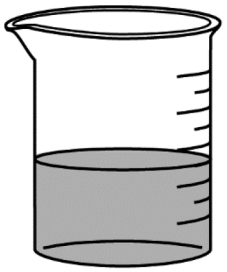
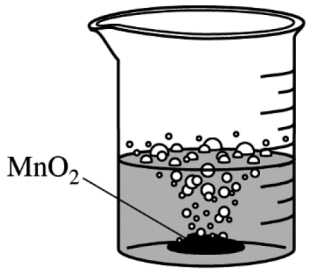
A student investigates the decomposition reaction in the laboratory. The student prepares two small beakers, adding 20.0 mL of 9.77 *M* $H_2O_2(aq)$ to each one. Each beaker is placed on an electronic balance. The student adds 0.10 g of $MnO_2(s)$ to the second beaker and records the mass of each beaker and its contents at 10-second intervals for one minute. The beakers and the data are shown below.



Beaker 1



Beaker 2

Time (seconds)	Mass of Beaker 1 + $H_2O_2(aq)$ (grams)	Mass of Beaker 2 + $H_2O_2(aq)$ + $MnO_2(s)$ (grams)
0	43.09	43.19
10	43.09	43.06
20	43.09	42.94
30	43.09	42.83
40	43.09	42.73
50	43.09	42.65
60	43.09	42.58

(c) For beaker 2 during the 60-second period, calculate the following.

(i) The number of moles of $O_2(g)$ that was produced

(ii) The mass of $H_2O_2(aq)$ that decomposed

(d) The student continues the experiment for an additional minute. For beaker 2, will the mass of $H_2O_2(aq)$ consumed during the second minute be greater than, less than, or equal to the mass of $H_2O_2(aq)$ consumed during the first minute? Explain your answer referring to the data in the table.

(e) Based on the data, the student claims that the catalyzed reaction has zeroth-order kinetics. Do you agree with the student's claim? Justify your answer.

(f) A second student did the experiment using larger volumes of 9.77 *M* $H_2O_2(aq)$. The student noticed that the reaction in beaker 2 proceeded extremely rapidly, causing some of the liquid to splash out of the beaker onto the lab table. The student claims that as a result of the loss of the liquid from the beaker, the calculated number of moles of $O_2(g)$ produced is greater than the actual number of moles of $O_2(g)$ produced during the first 60 seconds. Do you agree with the student? Justify your answer.

(g) The hydrogen peroxide used in this experiment can be prepared by the reaction of solid ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, with water. The products are hydrogen peroxide (H_2O_2) and ammonium bisulfate (NH_4HSO_4). Write the balanced equation for the reaction.

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PAGE FOR ANSWERING QUESTION 2

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

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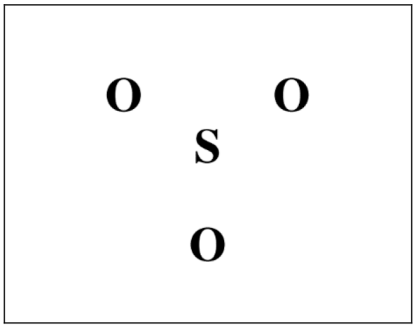
3. Sulfur trioxide, SO_3, is commercially produced on a massive scale for use in manufacturing. It is also produced as a by-product of burning fossil fuels and is an air pollutant involved in the formation of acid rain.

(a) In the box below, complete one of the valid Lewis electron-dot diagrams for the SO_3 molecule. Be sure to include all valence electrons, including lone pairs.



(b) Predict the shape of the SO_3 molecule based on the diagram you completed above.

Under some conditions, $SO_3(g)$ decomposes to produce $SO_2(g)$ and $O_2(g)$, as represented by the equation below.

$$2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g) \qquad \Delta H^\circ = 180\ \text{kJ/mol}_{rxn}$$

(c) Under what temperature conditions will the reaction be thermodynamically favored: high temperatures, low temperatures, all temperatures, or no temperatures? Justify your answer in terms of the change in enthalpy and the change in entropy during the reaction.

A chemist fills a rigid vessel with $SO_3(g)$ at a certain temperature until the pressure of $SO_3(g)$ in the container is 0.83 atm. The $SO_3(g)$ decomposes as the partial pressures of $SO_3(g)$, $SO_2(g)$, and $O_2(g)$ in the container are monitored over time, as shown in the following graph. A change is made to the system at time t_1.

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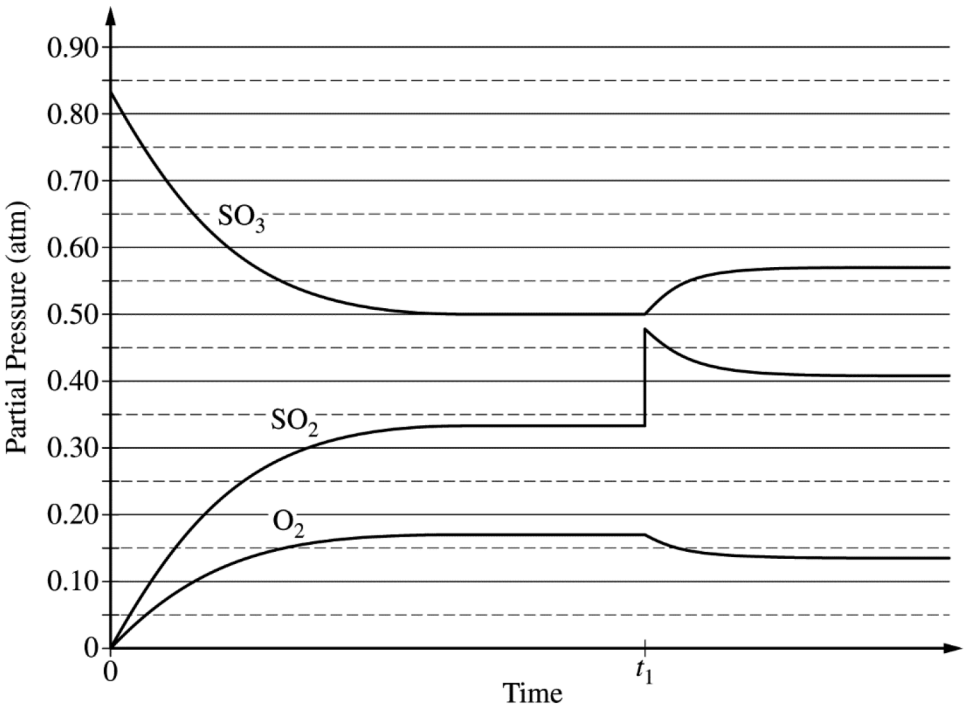

(d) Answer the following based on the graph.

(i) Draw an X on the time axis to show when the system first reached equilibrium.

(ii) Describe the change that was made to the system at time ty.

(iii) After the change was made at time t_1, the partial pressure of $SO_3(g)$ increased while the partial pressure of $O_2(g)$ decreased. Explain this observation.

(e) Use the information above to answer the following.

(i) Write the expression for the equilibrium constant, K_p, for the reaction.

(ii) Determine the value of K_p for the reaction.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

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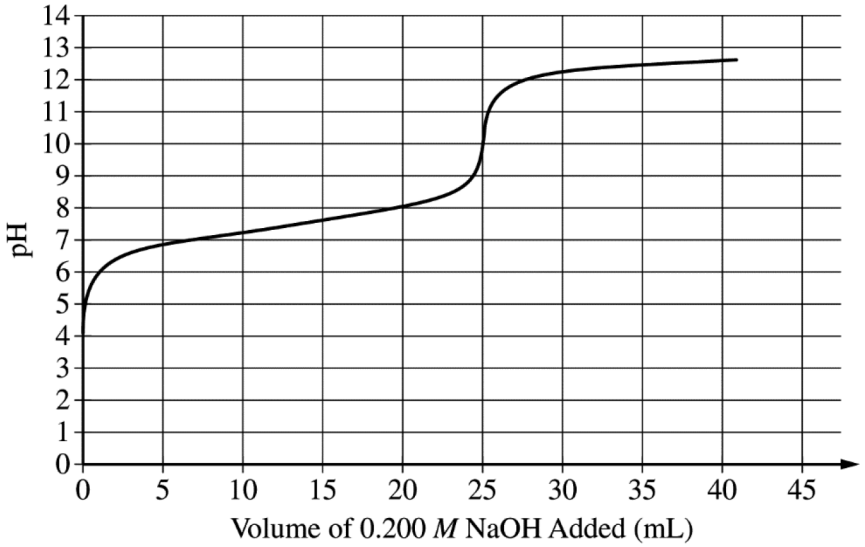
$$HClO(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + ClO^-(aq)$$

4. The reaction between hypochlorous acid and water is represented above.

(a) Identify one of the conjugate acid-base pairs in the reaction.

(b) Shown in the graph below is the titration curve that results when 25.0 mL of 0.200 *M* HClO is titrated with 0.200 *M* NaOH. Carefully draw a second curve on the graph that would result from the titration of 25.0 mL of 0.200 *M* $HClO_4$ with 0.200 *M* NaOH.



(c) A student proposes creating a buffer by dissolving 0.010 mol of $NaClO_4(s)$ in 100. mL of 0.100 *M* $HClO_4$. Explain why the resulting solution would not be a buffer.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 4

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Half-Reaction	E° (V)
$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$	$+0.815$
$NAD^+ + H^+ + 2\,e^- \rightarrow NADH$	-0.320

5. In human cells a compound known as NADH is involved in a reaction that generates an electrical potential. The reaction is based on the two half-reactions shown in the table above. The balanced equation for the overall reaction is shown below.

$$O_2 + 2\,H^+ + 2\,NADH \rightarrow 2\,H_2O + 2\,NAD^+$$

(a) How many moles of electrons are transferred for each mole of O_2 that reacts? Justify your answer in terms of the balanced equation and the change in oxidation number of oxygen.

(b) Calculate the electrochemical potential of the overall reaction.

(c) Calculate the value of ΔG° for the overall reaction.

(d) When the concentration of NADH increases while the concentration of NAD^+ decreases, will the electrochemical potential increase, decrease, or remain the same? Justify your answer.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 5

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6. Some building materials contain small capsules filled with paraffin wax to improve the insulating properties of the materials. The melting and freezing of paraffin inside the capsules in the material helps to regulate temperature. Paraffin wax begins to melt at 37°C.

(a) While the wax is melting, is the net flow of thermal energy from the wax to the surroundings or from the surroundings to the wax? Justify your answer.

(b) Calculate the amount of thermal energy, in kJ, that is required to melt 15.2 grams of solid paraffin wax when the temperature of the surroundings is above the melting point of paraffin. (The molar mass of paraffin is 282.62 g/mol, and its molar heat of fusion is 48.78 kJ/mol.)

(c) When paraffin wax melts, its density decreases. Provide a particle-level explanation of this observation.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 6

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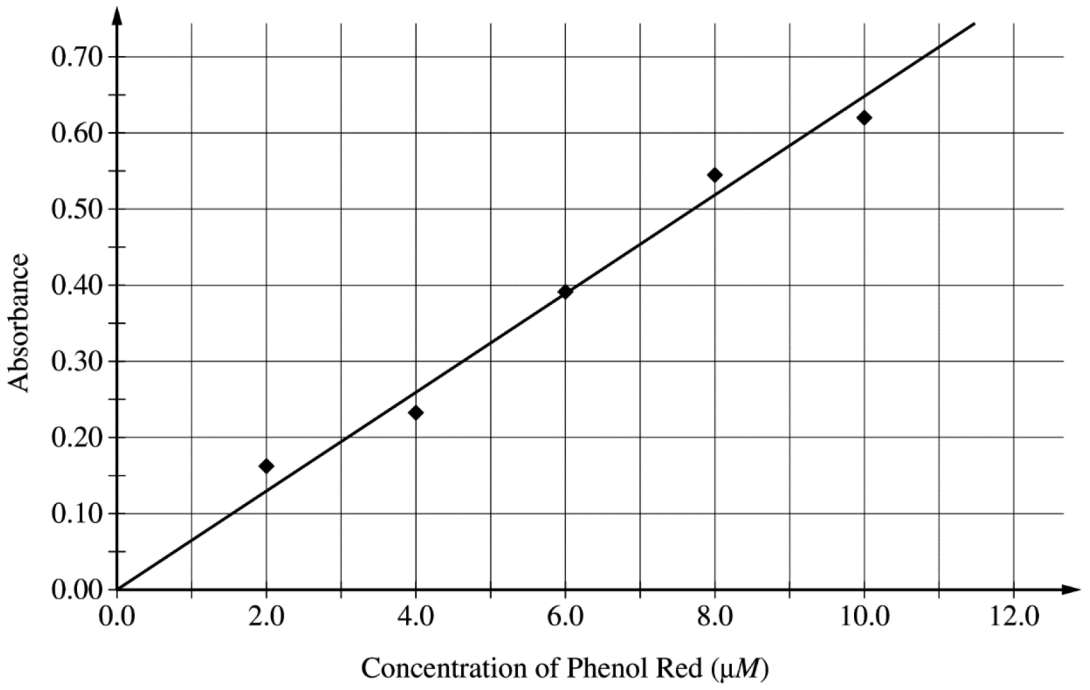
7. A student is given a solution of phenol red of unknown concentration. Solutions of phenol red are bright pink under basic conditions.

(a) The student uses a pH probe and determines that the pH of the solution is 11.20. Calculate the hydrogen ion concentration, $[H^+]$, in the solution of phenol red.

The student analyzes a sample of the solution using a spectrophotometer set at a wavelength of 559 nm, the wavelength of maximum absorbance for phenol red. The measured absorbance of the phenol red solution at 559 nm is 0.35.

(b) Based on the calibration curve shown below, what is the concentration of the solution in micromoles per liter (μM) ?



(c) If the student mixed 10 mL of distilled water with 10 mL of the sample, would this diluted solution have an absorbance greater than, less than, or equal to the absorbance of the original solution? Justify your answer.

(d) If the student measured the absorbance of the solution at a wavelength of 650 nm, would the absorbance be greater than, less than, or equal to the absorbance of the solution at 559 nm? Justify your answer.

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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 mol^{-1} K^{-1}
= 0.08206 L atm mol^{-1} K^{-1}
= 62.36 L torr mol^{-1} K^{-1}

1 atm = 760 mm Hg = 760 torr

STP = 273.15 K and 1.0 atm

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

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

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

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

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

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