CHEMISTRY
Section I
60 Multiple-Choice Questions
(Time—90 minutes)
YOU MAY NOT USE YOUR CALCULATOR FOR SECTION I

Note: For all questions, assume that the temperature is 298 K, the pressure is 1.00 atmosphere, 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 answer that is best in each case and then fill in the corresponding circle on the answer sheet.

1. Complete combustion of a sample of a hydrocarbon in excess oxygen produces equimolar quantities of carbon dioxide and water. Which of the following could be the molecular formula of the compound?

   (A) C_2H_2
   (B) C_2H_6
   (C) C_4H_8
   (D) C_6H_6

Substance	Equilibrium Vapor Pressure at 20°C (torr)
$C_6H_6(l)$	75
$C_2H_5OH(l)$	44
$CH_3OH(l)$	92
$C_2H_6O_2(l)$	0.06

2. Based on the data in the table above, which of the following liquid substances has the weakest intermolecular forces?

   (A) $C_6H_6(l)$
   (B) $C_2H_5OH(l)$
   (C) $CH_3OH(l)$
   (D) $C_2H_6O_2(l)$

Ion	Ionic Radius (pm)
Zn^{2+}	74
Ca^{2+}	100
Ba^{2+}	135

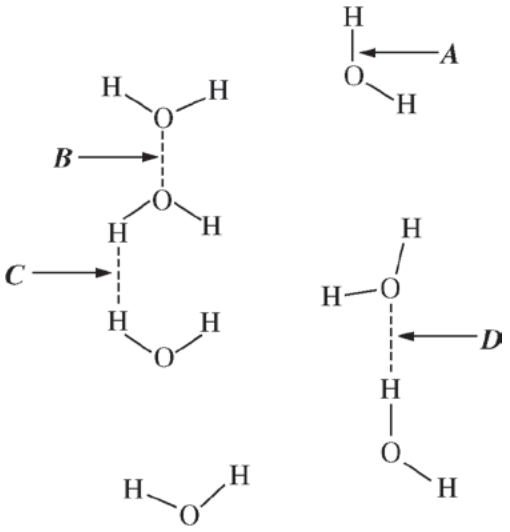
3. Based on the data in the table above, which of the following correctly predicts the relative strength of the attraction of Zn^{2+}, Ca^{2+}, and Ba^{2+} ions to water molecules in a solution, from strongest to weakest, and provides the correct reason?

   (A) $Zn^{2+} > Ca^{2+} > Ba^{2+}$ because the smaller ions have a stronger coulombic attraction to water
   (B) $Zn^{2+} > Ca^{2+} > Ba^{2+}$ because the smaller ions are more electronegative
   (C) $Ba^{2+} > Ca^{2+} > Zn^{2+}$ because the larger ions are more polarizable
   (D) $Ba^{2+} > Ca^{2+} > Zn^{2+}$ because the larger ions are less electronegative

4. $Zn(s)$ is used to reduce other compounds in chemical reactions. If a chemist needs a substance that is more effective in its reducing ability, which of the following species would be the best choice?

   (A) Na
   (B) H^+
   (C) K^+
   (D) Cl^-

GO ON TO THE NEXT PAGE.



5. In the diagram above, which of the labeled arrows identifies hydrogen bonding in water?

   (A) ***A***
   (B) ***B***
   (C) ***C***
   (D) ***D***

6. A kinetics experiment is set up to collect the gas that is generated when a sample of chalk, consisting primarily of solid $CaCO_3$, is added to a solution of ethanoic acid, CH_3COOH. The rate of reaction between $CaCO_3$ and CH_3COOH is determined by measuring the volume of gas generated at 25°C and 1 atm as a function of time. Which of the following experimental conditions is most likely to increase the rate of gas production?

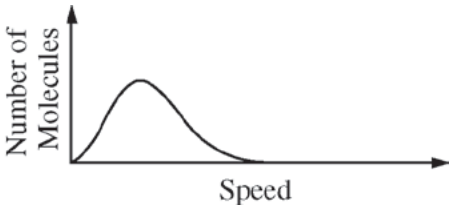
   (A) Decreasing the volume of ethanoic acid solution used in the experiment
   (B) Decreasing the concentration of the ethanoic acid solution used in the experiment
   (C) Decreasing the temperature at which the experiment is performed
   (D) Decreasing the particle size of the $CaCO_3$ by grinding it into a fine powder

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

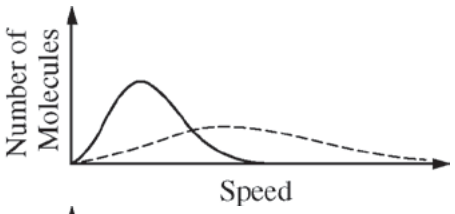
7. At 450°C, 2.0 moles each of $H_2(g)$, $I_2(g)$, and $HI(g)$ are combined in a 1.0 L rigid container. The value of K_c at 450°C is 50. Which of the following will occur as the system moves toward equilibrium?

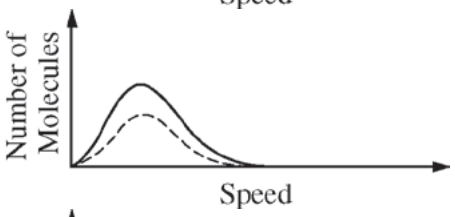
   (A) More $H_2(g)$ and $I_2(g)$ will form.
   (B) More $HI(g)$ will form.
   (C) The total pressure will decrease.
   (D) No net reaction will occur, because the number of molecules is the same on both sides of the equation.

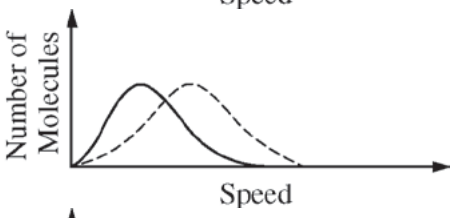
GO ON TO THE NEXT PAGE.

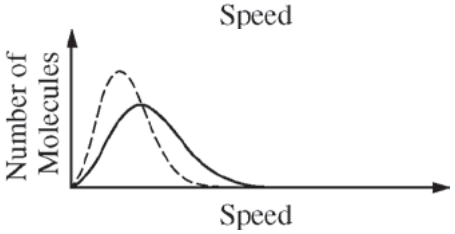


8. The graph above shows the speed distribution of molecules in a sample of a gas at a certain temperature. Which of the following graphs shows the speed distribution of the same molecules at a lower temperature (as a dashed curve) ?

(A)


(B)


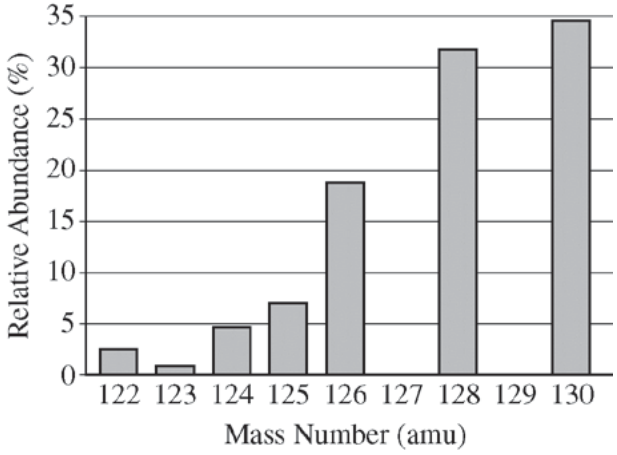
(C)


(D)


9. A 100 g sample of a metal was heated to 100°C and then quickly transferred to an insulated container holding 100 g of water at 22°C. The temperature of the water rose to reach a final temperature of 35°C. Which of the following can be concluded?

(A) The metal temperature changed more than the water temperature did; therefore the metal lost more thermal energy than the water gained.
(B) The metal temperature changed more than the water temperature did, but the metal lost the same amount of thermal energy as the water gained.
(C) The metal temperature changed more than the water temperature did; therefore the heat capacity of the metal must be greater than the heat capacity of the water.
(D) The final temperature is less than the average starting temperature of the metal and the water; therefore the total energy of the metal and water decreased.

GO ON TO THE NEXT PAGE.



10. The elements I and Te have similar average atomic masses. A sample that was believed to be a mixture of I and Te was run through a mass spectrometer, resulting in the data above. All of the following statements are true. Which one would be the best basis for concluding that the sample was pure Te?

    (A) Te forms ions with a −2 charge, whereas I forms ions with a −1 charge.
    (B) Te is more abundant than I in the universe.
    (C) I consists of only one naturally occurring isotope with 74 neutrons, whereas Te has more than one isotope.
    (D) I has a higher first ionization energy than Te does.

$$H_2C_2O_4(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HC_2O_4^-(aq)$$

$$HC_2O_4^-(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + C_2O_4^{2-}(aq)$$

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

11. All the reactions represented above occur in an aqueous solution of oxalic acid. Which of the following represent a Brønsted-Lowry conjugate acid-base pair?

    (A) $H_2C_2O_4(aq)$ and $C_2O_4^{2-}(aq)$
    (B) $HC_2O_4^-(aq)$ and $C_2O_4^{2-}(aq)$
    (C) $HC_2O_4^-(aq)$ and $H_2O(aq)$
    (D) $H_3O^+(aq)$ and $OH^-(aq)$

GO ON TO THE NEXT PAGE.

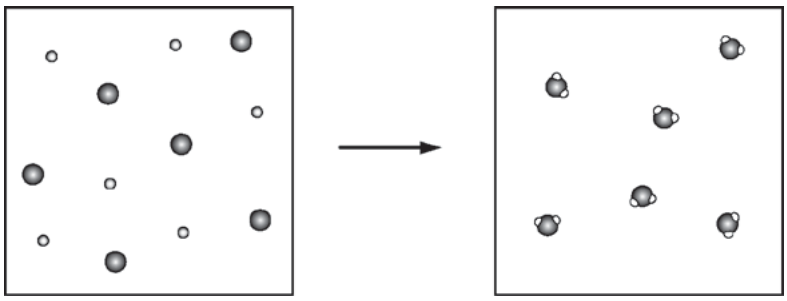
12. Which of the following reactions is not thermodynamically favored at low temperatures but becomes favored as the temperature increases?

	Reaction	$\Delta H°$ (kJ/mol$_{rxn}$)	$\Delta S°$ (J/(mol$_{rxn}$·K))
(A)	$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$	−566	−173
(B)	$2\ H_2O(g) \rightarrow 2\ H_2(g) + O_2(g)$	484	90.0
(C)	$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$	−164	149
(D)	$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2\ Cl^-(aq)$	23.4	−12.5

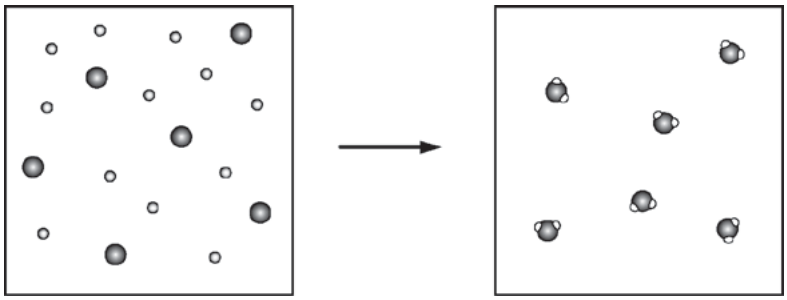
GO ON TO THE NEXT PAGE.

13. Which of the following particulate diagrams best shows the formation of water vapor from hydrogen gas and oxygen gas in a rigid container at 125°C ?

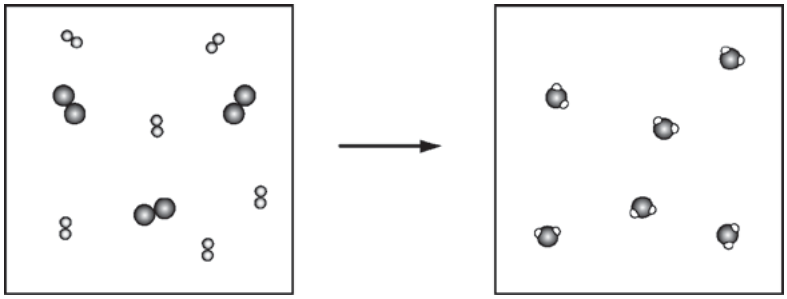
(A)



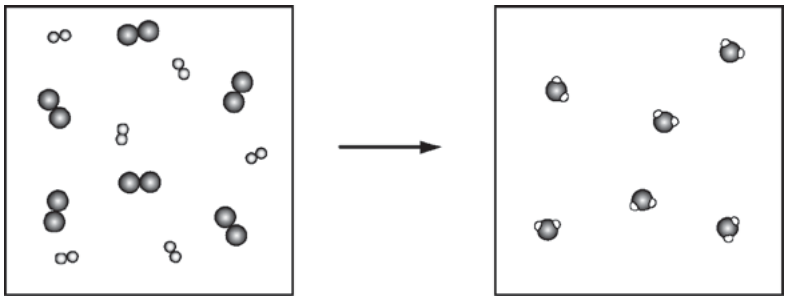
(B)



(C)

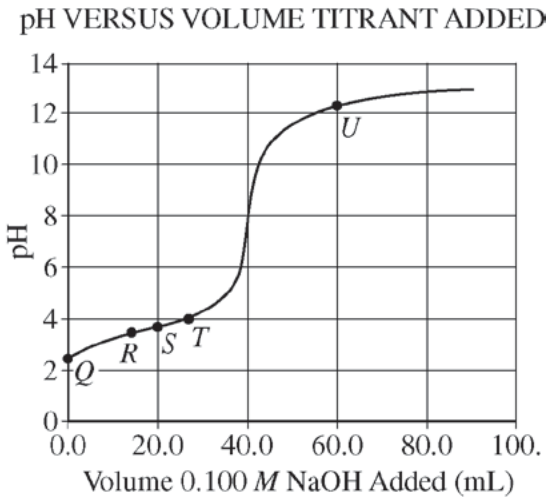


(D)



GO ON TO THE NEXT PAGE.

Questions 14-17 refer to the following.



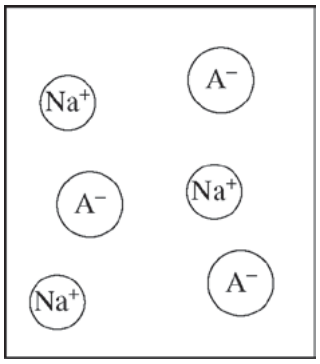
A 50.0 mL sample of an acid, HA, of unknown molarity is titrated, and the pH of the resulting solution is measured with a pH meter and graphed as a function of the volume of 0.100 *M* NaOH added.

14. At point *R* in the titration, which of the following species has the highest concentration?

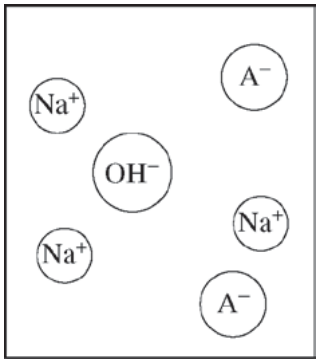
    (A) HA
    (B) A^-
    (C) H_3O^+
    (D) OH^-

15. Which of the following is the best particulate representation of the species (other than H_2O) that are present in significant concentrations in the solution at point *U* in the titration?

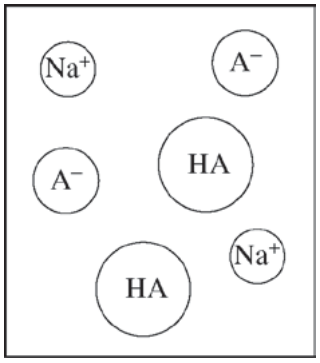
(A)



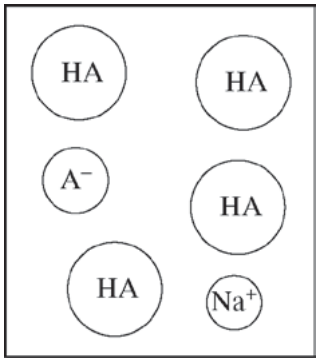
(B)



(C)



(D)



GO ON TO THE NEXT PAGE.

16. At which point on the titration curve is $[A^-]$ closest to twice that of [HA] ?

(A) *R*
(B) *S*
(C) *T*
(D) *U*

17. A student carries out the same titration, but uses an indicator instead of a pH meter. If the indicator changes color slightly past the equivalence point, what will the student obtain for the calculated concentration of the acid?

(A) Slightly less than 0.0800 *M*
(B) Slightly more than 0.0800 *M*
(C) Slightly less than 0.125 *M*
(D) Slightly more than 0.125 *M*

GO ON TO THE NEXT PAGE.

Questions 18-20 refer to three gases in identical rigid containers under the conditions given in the table below.

Container	A	B	C
Gas	Methane	Ethane	Butane
Formula	CH_4	C_2H_6	C_4H_{10}
Molar mass (g/mol)	16	30.	58
Temperature (°C)	27	27	27
Pressure (atm)	2.0	4.0	2.0

18. The average kinetic energy of the gas molecules is

(A) greatest in container A
(B) greatest in container B
(C) greatest in container C
(D) the same in all three containers

19. The density of the gas, in g/L, is

(A) greatest in container A
(B) greatest in container B
(C) greatest in container C
(D) the same in all three containers

20. If the pressure of each gas is increased at constant temperature until condensation occurs, which gas will condense at the lowest pressure?

(A) Methane
(B) Ethane
(C) Butane
(D) All the gases will condense at the same pressure.

---

21. The mass percent of carbon in pure glucose, $C_6H_{12}O_6$, is 40.0 percent. A chemist analyzes an impure sample of glucose and determines that the mass percent of carbon is 38.2 percent. Which of the following impurities could account for the low mass percent of carbon in the sample?

(A) Water, H_2O
(B) Ribose, $C_5H_{10}O_5$
(C) Fructose, $C_6H_{12}O_6$, an isomer of glucose
(D) Sucrose, $C_{12}H_{22}O_{11}$

22. Caffeine ($C_8H_{10}N_4O_2$) is a weak base with a K_b value of 4×10^{-4}. The pH of a 0.01 *M* solution of caffeine is in the range of

(A) 2–3
(B) 5–6
(C) 7–8
(D) 11–12

---

23. Lewis electron-dot diagrams for CO_2 and SO_2 are given above. The molecular geometry and polarity of the two substances are

(A) the same because the molecular formulas are similar
(B) the same because C and S have similar electronegativity values
(C) different because the lone pair of electrons on the S atom make it the negative end of a dipole
(D) different because S has a greater number of electron domains (regions of electron density) surrounding it than C has

$$2\ NO(g)\ +\ O_2(g) \rightarrow\ 2\ NO_2(g)$$

24. Consider the following mechanism for the reaction represented above.

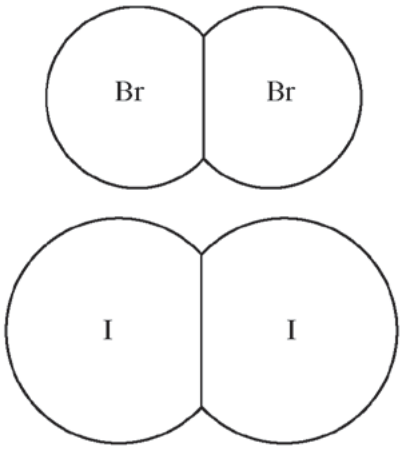
Step 1: $2\ NO \rightleftarrows N_2O_2$ (*fast reversible*)

Step 2: $N_2O_2 + O_2 \rightarrow 2\ NO_2$ (*slow*)

Which of the following statements is true?

(A) Step 1 represents a unimolecular reaction.
(B) Increasing the concentration of NO will decrease the overall rate of the reaction.
(C) Raising the temperature will have no effect on the numerical value of the rate constant.
(D) The rate law that is consistent with the mechanism is $rate = k[NO]^2[O_2]$.

GO ON TO THE NEXT PAGE.



25. The diagram above shows molecules of Br_2 and I_2 drawn to the same scale. Which of the following is the best explanation for the difference in the boiling points of liquid Br_2 and I_2, which are 59°C and 184°C, respectively?

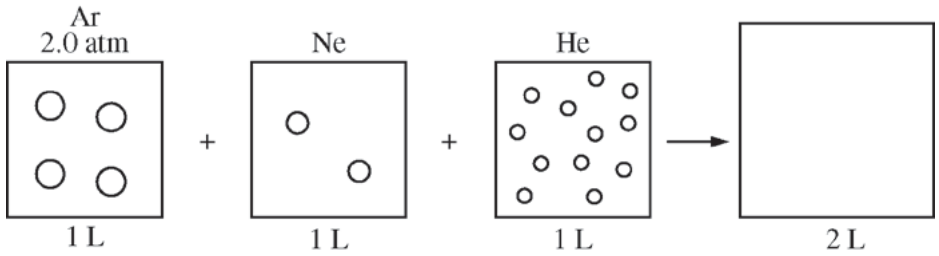
(A) Solid iodine is a network covalent solid, whereas solid bromine is a molecular solid.

(B) The covalent bonds in I_2 molecules are weaker than those in Br_2 molecules.

(C) I_2 molecules have electron clouds that are more polarizable than those of Br_2 molecules, thus London dispersion forces are stronger in liquid I_2.

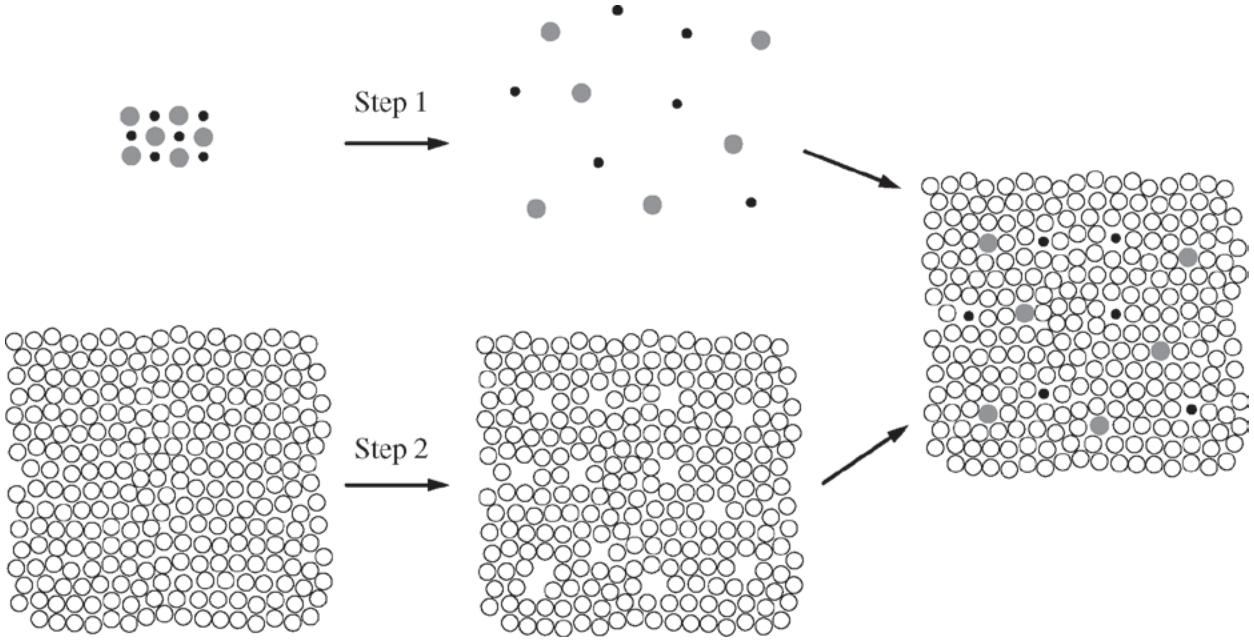
(D) Bromine has a greater electronegativity than iodine, thus there are stronger dipole-dipole forces in liquid bromine than in liquid iodine.

GO ON TO THE NEXT PAGE.



26. The figure above represents three sealed 1.0 L vessels, each containing a different inert gas at 298 K. The pressure of Ar in the first vessel is 2.0 atm. The ratio of the numbers of Ar, Ne, and He atoms in the vessels is 2:1:6, respectively. After all the gases are combined in a previously evacuated 2.0 L vessel, what is the total pressure of the gases at 298 K?

(A) 3.0 atm
(B) 4.5 atm
(C) 9.0 atm
(D) 18 atm



27. The dissolution of an ionic solute in a polar solvent can be imagined as occurring in three steps, as shown in the figure above. In step 1, the separation between ions in the solute is greatly increased, just as will occur when the solute dissolves in the polar solvent. In step 2, the polar solvent is expanded to make spaces that the ions will occupy. In the last step, the ions are inserted into the spaces in the polar solvent. Which of the following best describes the enthalpy change, ΔH, for each step?

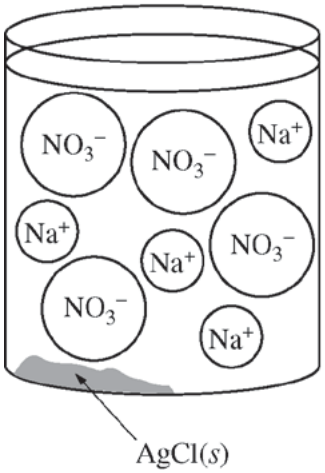
(A) All three steps are exothermic.
(B) All three steps are endothermic.
(C) Steps 1 and 2 are exothermic, and the final step is endothermic.
(D) Steps 1 and 2 are endothermic, and the final step is exothermic.

GO ON TO THE NEXT PAGE.

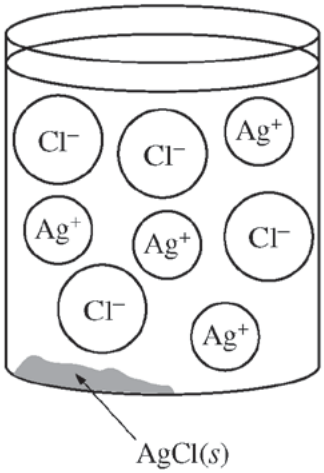
$$Ag^+(aq) + Cl^-(aq) \rightleftarrows AgCl(s)$$

28. A student mixes dilute $AgNO_3(aq)$ with excess $NaCl(aq)$ to form $AgCl(s)$, as represented by the net ionic equation above. Which of the diagrams below best represents the ions that are present in significant concentrations in the solution? (K_{sp} for AgCl is 1.8×10^{-10}.)

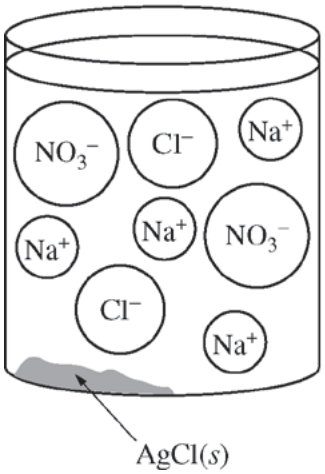
(A)



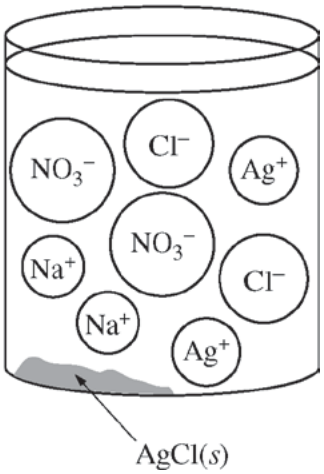
(B)



(C)



(D)



GO ON TO THE NEXT PAGE.

Questions 29-33 refer to the following.

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

$PCl_5(g)$ decomposes into $PCl_3(g)$ and $Cl_2(g)$ according to the equation above. A pure sample of $PCl_5(g)$ is placed in a rigid, evacuated 1.00 L container. The initial pressure of the $PCl_5(g)$ is 1.00 atm. The temperature is held constant until the $PCl_5(g)$ reaches equilibrium with its decomposition products. The figures below show the initial and equilibrium conditions of the system.

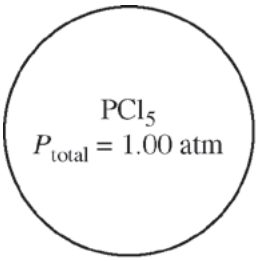


Figure 1: Initial

Figure 2: Equilibrium

29. Which of the following is the most likely cause for the increase in pressure observed in the container as the reaction reaches equilibrium?

(A) A decrease in the strength of intermolecular attractions among molecules in the flask
(B) An increase in the strength of intermolecular attractions among molecules in the flask
(C) An increase in the number of molecules, which increases the frequency of collisions with the walls of the container
(D) An increase in the speed of the molecules that then collide with the walls of the container with greater force

30. As the reaction progresses toward equilibrium, the rate of the forward reaction

(A) increases until it becomes the same as the reverse reaction rate at equilibrium
(B) stays constant before and after equilibrium is reached
(C) decreases to become a constant nonzero rate at equilibrium
(D) decreases to become zero at equilibrium

31. If the decomposition reaction were to go to completion, the total pressure in the container would be

(A) 1.4 atm
(B) 2.0 atm
(C) 2.8 atm
(D) 3.0 atm

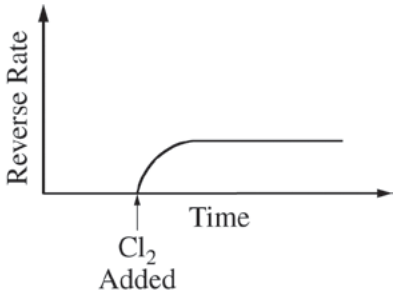
GO ON TO THE NEXT PAGE.

32. Which of the following statements about K_p, the equilibrium constant for the reaction, is correct?

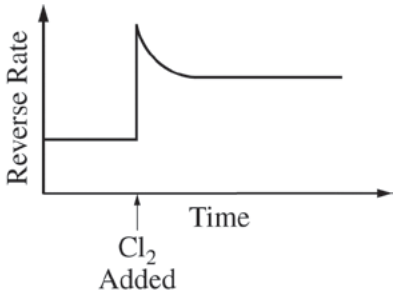
(A) $K_p > 1$
(B) $K_p < 1$
(C) $K_p = 1$
(D) It cannot be determined whether $K_p > 1$, $K_p < 1$, or $K_p = 1$ without additional information.

33. Additional $Cl_2(g)$ is injected into the system at equilibrium. Which of the following graphs best shows the rate of the reverse reaction as a function of time? (Assume that the time for injection and mixing of the additional $Cl_2(g)$ is negligible.)

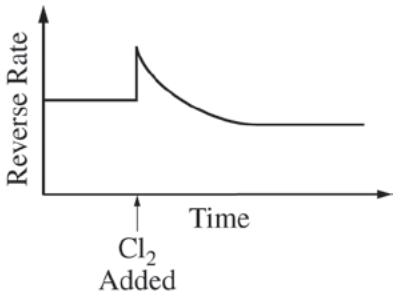
(A)



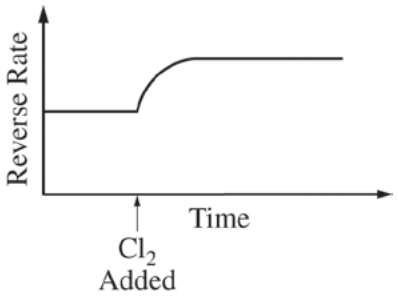
(B)



(C)



(D)



GO ON TO THE NEXT PAGE.

Questions 34-38

$$K(s) + \frac{1}{2}Cl_2(g) \rightarrow KCl(s) \qquad \Delta H^\circ = -437 \text{ kJ/mol}_{rxn}$$

The elements K and Cl react directly to form the compound KCl according to the equation above. Refer to the information above and the table below to answer the questions that follow.

Process	ΔH° (kJ/mol_{rxn})
$K(s) \rightarrow K(g)$	v
$K(g) \rightarrow K^+(g) + e^-$	w
$Cl_2(g) \rightarrow 2\,Cl(g)$	x
$Cl(g) + e^- \rightarrow Cl^-(g)$	y
$K^+(g) + Cl^-(g) \rightarrow KCl(s)$	z

34. How much heat is released or absorbed when 0.050 mol of $Cl_2(g)$ is formed from $KCl(s)$?

(A) 87.4 kJ is released
(B) 43.7 kJ is released
(C) 43.7 kJ is absorbed
(D) 87.4 kJ is absorbed

35. What remains in the reaction vessel after equal masses of $K(s)$ and $Cl_2(g)$ have reacted until either one or both of the reactants have been completely consumed?

(A) KCl only
(B) KCl and K only
(C) KCl and Cl_2 only
(D) KCl, K, and Cl_2

36. Which of the values of ΔH° for a process in the table is (are) less than zero (i.e., indicate(s) an exothermic process) ?

(A) z only
(B) y and z only
(C) x, y, and z only
(D) w, x, y, and z

37. It is observed that the reaction producing KCl from its elements goes essentially to completion. Which of the following is a true statement about the thermodynamic favorability of the reaction?

(A) The reaction is favorable and driven by an enthalpy change only.
(B) The reaction is unfavorable and driven by an entropy change only.
(C) The reaction is favorable and driven by both enthalpy and entropy changes.
(D) The reaction is unfavorable due to both enthalpy and entropy changes.

$$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(g)$$

38. Which of the following expressions is equivalent to ΔH° for the reaction represented above?

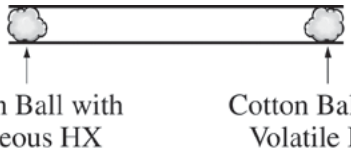
(A) $x + y$

(B) $x - y$

(C) $x + 2y$

(D) $\frac{x}{2} - y$

GO ON TO THE NEXT PAGE.



39. The experimental apparatus represented above is used to demonstrate the rates at which gases diffuse. When the cotton balls are placed in the ends of a tube at the same time, the gases diffuse from each end and meet somewhere in between, where they react to form a white solid. Which of the following combinations will produce a solid closest to the center of the tube?

    (A) HCl and CH_3NH_2

    (B) HCl and NH_3

    (C) HBr and CH_3NH_2

    (D) HBr and NH_3

40. Silicon crystals are semiconductors. Which of the following is a correct reason for the increase in the conductivity of Si crystals when a small fraction of Si atoms are replaced with those of a different element?

    (A) P atoms introduce additional mobile negative charges.
    (B) P atoms introduce additional mobile positive charges.
    (C) Ge atoms have more electrons than Si atoms have.
    (D) Ge atoms are much smaller than Si atoms.

41. N_2 molecules absorb ultraviolet light but not visible light. I_2 molecules absorb both visible and ultraviolet light. Which of the following statements explains the observations?

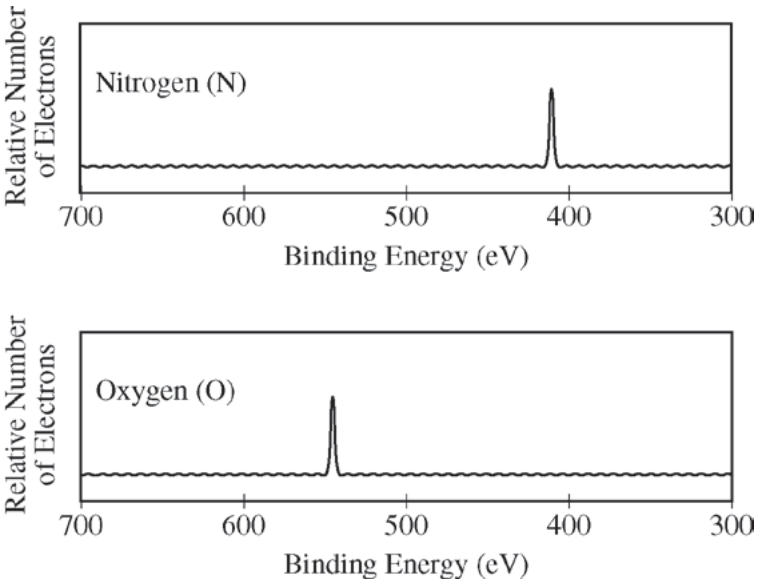
    (A) More energy is required to make N_2 molecules vibrate than is required to make I_2 molecules vibrate.
    (B) More energy is required to remove an electron from an I_2 molecule than is required to remove an electron from a N_2 molecule.
    (C) Visible light does not produce transitions between electronic energy levels in the N_2 molecule but does produce transitions in the I_2 molecule.
    (D) The molecular mass of I_2 is greater than the molecular mass of N_2.

Element	Metallic Radius (pm)	Melting Point (°C)	Common Oxidation State
Au	144	1064	1+, 3+
Cu	128	1085	1+, 2+
Ag	144	961	1+

42. To make Au stronger and harder, it is often alloyed with other metals, such as Cu and Ag. Consider two alloys, one of Au and Cu and one of Au and Ag, each with the same mole fraction of Au. If the Au/Cu alloy is harder than the Au/Ag alloy, then which of the following is the best explanation based on the information in the table above?

    (A) Cu has two common oxidation states, but Ag has only one.
    (B) Cu has a higher melting point than Au has, but Ag has a lower melting point than Au has.
    (C) Cu atoms are smaller than Ag atoms, thus they interfere more with the displacement of atoms in the alloy.
    (D) Cu atoms are less polarizable than are Au or Ag atoms, thus Cu has weaker interparticle forces.

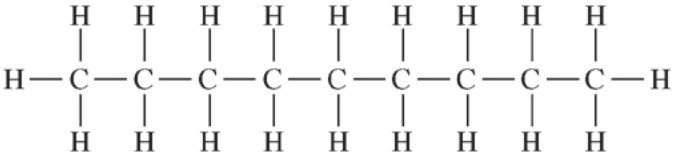
GO ON TO THE NEXT PAGE.



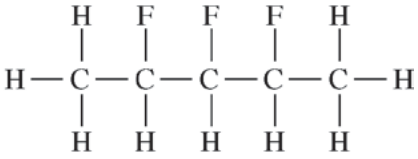
43. The photoelectron spectra above show the energy required to remove a 1*s* electron from a nitrogen atom and from an oxygen atom. Which of the following statements best accounts for the peak in the upper spectrum being to the right of the peak in the lower spectrum?

(A) Nitrogen atoms have a half-filled *p* subshell.
(B) There are more electron-electron repulsions in oxygen atoms than in nitrogen atoms.
(C) Electrons in the *p* subshell of oxygen atoms provide more shielding than electrons in the *p* subshell of nitrogen atoms.
(D) Nitrogen atoms have a smaller nuclear charge than oxygen atoms.

GO ON TO THE NEXT PAGE.



Nonane



2,3,4-trifluoropentane

44. Consider the molecules represented above and the data in the table below.

Compound	Molecular Formula	Molar Mass (g/mol)	Boiling Point (°C)
Nonane	C_9H_{20}	128	151
2,3,4-trifluoropentane	$C_5H_9F_3$	126	89

Nonane and 2,3,4-trifluoropentane have almost identical molar masses, but nonane has a significantly higher boiling point. Which of the following statements best helps explain this observation?

(A) The C–F bond is easier to break than the C–H bond.
(B) The C–F bond is more polar than the C–H bond.
(C) The carbon chains are longer in nonane than they are in 2,3,4-trifluoropentane.
(D) The carbon chains are farther apart in a sample of nonane than they are in 2,3,4-trifluoropentane.

GO ON TO THE NEXT PAGE.

Questions 45-47 refer to galvanic cells made from different combinations of the three half-cells described below.

Half-cell 1: strip of Al(s) in 1.00 M $Al(NO_3)_3(aq)$
Half-cell 2: strip of Cu(s) in 1.00 M $Cu(NO_3)_2(aq)$
Half-cell 3: strip of Fe(s) in 1.00 M $Fe(NO_3)_2(aq)$

Galvanic Cell	Half-cells	Cell Reaction	E°_{cell} (V)
X	1 and 2	$2\ Al(s) + 3\ Cu^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cu(s)$	2.00
Y	1 and 3	$2\ Al(s) + 3\ Fe^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Fe(s)$	1.22
Z	2 and 3	$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$	?

45. What is the standard cell potential of galvanic cell Z?

(A) 0.26 V
(B) 0.78 V
(C) 2.34 V
(D) 3.22 V

46. In galvanic cells Y and Z, which of the following takes place in half-cell 3 ?

(A) Reduction occurs in both cell Y and cell Z.
(B) Oxidation occurs in both cell Y and cell Z.
(C) Reduction occurs in cell Y, and oxidation occurs in cell Z.
(D) Oxidation occurs in cell Y, and reduction occurs in cell Z.

47. If the half-cell containing 1.00 M $Fe(NO_3)_2(aq)$ in galvanic cells Y and Z is replaced with a half-cell containing 5.00 M $Fe(NO_3)_2(aq)$, what will be the effect on the cell voltage of the two galvanic cells?

(A) The voltage will increase in both cells.
(B) The voltage will decrease in both cells.
(C) The voltage will increase in cell Y and decrease in cell Z.
(D) The voltage will decrease in cell Y and increase in cell Z.

GO ON TO THE NEXT PAGE.

Questions 48-52 refer to the following.

Concentration (*M*)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

The pH of solutions of four acids prepared at various concentrations were measured and recorded in the table above. The four acids are, in no particular order, chlorous, hydrochloric, lactic, and propanoic.

48. For which acid is the value of the acid-dissociation constant, K_a, the smallest?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) Acid 4

49. Which of the four acids listed in the table is hydrochloric acid?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) Acid 4

50. Of the following species, which has the greatest concentration in a 1.0 *M* solution of acid 1 at equilibrium?

(A) OH^-
(B) H_3O^+
(C) Acid 1
(D) The conjugate base of acid 1

51. If equal volumes of the four acids at a concentration of 0.50 *M* are each titrated with a strong base, which will require the greatest volume of base to reach the equivalence point?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) All the acids will require the same volume of base to reach the equivalence point.

52. A 25 mL sample of a 1.0 *M* solution of acid 1 is mixed with 25 mL of 0.50 *M* NaOH. Which of the following best explains what happens to the pH of the mixture when a few drops of 1.0 *M* HNO_3 are added?

(A) The pH of the mixture increases sharply, because HNO_3 is a strong acid.
(B) The pH of the mixture decreases sharply, because H_3O^+ ions were added.
(C) The pH of the mixture stays about the same, because the conjugate base of acid 1 reacts with the added H_3O^+ ions.
(D) The pH of the mixture stays about the same, because the OH^- ions in the solution react with the added H_3O^+ ions.

GO ON TO THE NEXT PAGE.

Step 1: $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$

Step 2: $ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$

53. A proposed mechanism for destruction of ozone gas in the stratosphere is represented above. Which of the following is evidence that the mechanism is occurring?

(A) The presence of $Cl(g)$ increases the rate of the overall reaction.

(B) The presence of $Cl(g)$ decreases the rate of the overall reaction.

(C) The presence of $Cl(g)$ increases the equilibrium constant of the overall reaction.

(D) The presence of $Cl(g)$ decreases the equilibrium constant of the overall reaction.

GO ON TO THE NEXT PAGE.

	NaF	MgO
Boiling Point (°C)	1695	3600

	Na^+	Mg^{2+}	F^-	Cl^-	O^{2-}
Ionic Radius (pm)	76	72	133	181	140

54. Based on the data in the tables above, which of the following statements provides the best prediction for the boiling point of NaCl ?

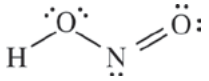
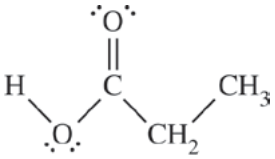
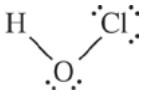
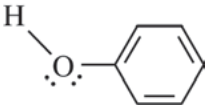
(A) NaCl will have a lower boiling point than NaF because the coulombic attractions are weaker in NaCl than in NaF.

(B) NaCl will have a boiling point between that of NaF and MgO because the covalent character of the bonds in NaCl is intermediate between that of MgO and NaF.

(C) NaCl will have a higher boiling point than MgO because the ions are spaced farther apart in NaCl.

(D) NaCl will have a higher boiling point than MgO because the energy required to transfer electrons from the anion to the cation is larger in NaCl than in MgO.

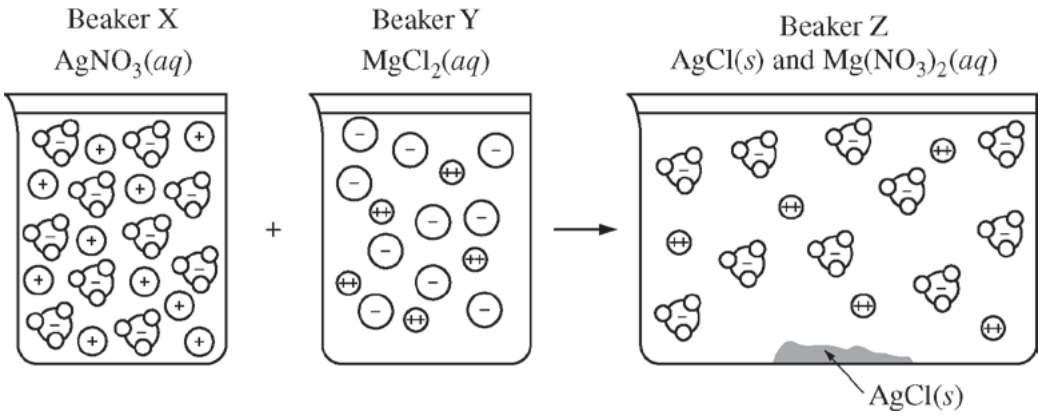
GO ON TO THE NEXT PAGE.

Acid	Structure	K_a
HNO_2		4.0×10^{-4}
$HC_3H_5O_2$		1.3×10^{-5}
HClO		3.0×10^{-8}
HOC_6H_5		1.6×10^{-10}

55. The table above shows the values of K_a for four weak acids. Which of the following pairs of chemical species, when combined in equimolar amounts, results in a buffer with a pH closest to 7.5 ?

(A) HNO_2 and OH^-
(B) $HC_3H_5O_2$ and $C_3H_5O_2^-$
(C) HClO and ClO^-
(D) C_6H_5OH and $C_6H_5O^-$

GO ON TO THE NEXT PAGE.



56. Beaker X and beaker Y each contain 1.0 L of solution, as shown above. A student combines the solutions by pouring them into a larger, previously empty beaker Z and observes the formation of a white precipitate. Assuming that volumes are additive, which of the following sets of solutions could be represented by the diagram above?

	Beaker X	Beaker Y	Beaker Z
(A)	2.0 *M* $AgNO_3$	2.0 *M* $MgCl_2$	4.0 *M* $Mg(NO_3)_2$ and $AgCl(s)$
(B)	2.0 *M* $AgNO_3$	2.0 *M* $MgCl_2$	2.0 *M* $Mg(NO_3)_2$ and $AgCl(s)$
(C)	2.0 *M* $AgNO_3$	1.0 *M* $MgCl_2$	1.0 *M* $Mg(NO_3)_2$ and $AgCl(s)$
(D)	2.0 *M* $AgNO_3$	1.0 *M* $MgCl_2$	0.50 *M* $Mg(NO_3)_2$ and $AgCl(s)$

GO ON TO THE NEXT PAGE.

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

57. A sample of N_2O_5 was placed in an evacuated container, and the reaction represented above occurred. The value of $P_{N_2O_5}$, the partial pressure of $N_2O_5(g)$, was measured during the reaction and recorded in the table below.

Time (min)	$P_{N_2O_5}$ (atm)	$\ln(P_{N_2O_5})$	$\frac{1}{P_{N_2O_5}}$ (atm^{-1})
0	150	5.0	0.0067
100	75	4.3	0.013
200	38	3.6	0.027
300	19	2.9	0.053

Which of the following correctly describes the reaction?

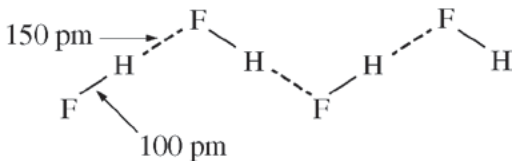
(A) The decomposition of N_2O_5 is a zero-order reaction.
(B) The decomposition of N_2O_5 is a first-order reaction.
(C) The decomposition of N_2O_5 is a second-order reaction.
(D) The overall reaction order is 3.

Element	Atomic Radius	First Ionization Energy
Calcium	194 pm	590 kJ/mol
Potassium	—	—

58. Based on periodic trends and the data in the table above, which of the following are the most probable values of the atomic radius and the first ionization energy for potassium, respectively?

(A) 242 pm, 633 kJ/mol
(B) 242 pm, 419 kJ/mol
(C) 120 pm, 633 kJ/mol
(D) 120 pm, 419 kJ/mol

GO ON TO THE NEXT PAGE.



59. The figure above shows that in solid hydrogen fluoride there are two different distances between H atoms and F atoms. Which of the following best accounts for the two different distances?

(A) Accommodation of the necessary bond angles in the formation of the solid
(B) Difference in strength between covalent bonds and intermolecular attractions
(C) Different isotopes of fluorine present in the samples
(D) Uneven repulsions among nonbonding electron pairs

$$COCl_2(g) \rightleftarrows CO(g) + Cl_2(g)$$

60. $COCl_2(g)$ decomposes according to the equation above. When pure $COCl_2(g)$ is injected into a rigid, previously evacuated flask at 690 K, the pressure in the flask is initially 1.0 atm. After the reaction reaches equilibrium at 690 K, the total pressure in the flask is 1.2 atm. What is the value of K_p for the reaction at 690 K?

(A) 0.040
(B) 0.050
(C) 0.80
(D) 1.0

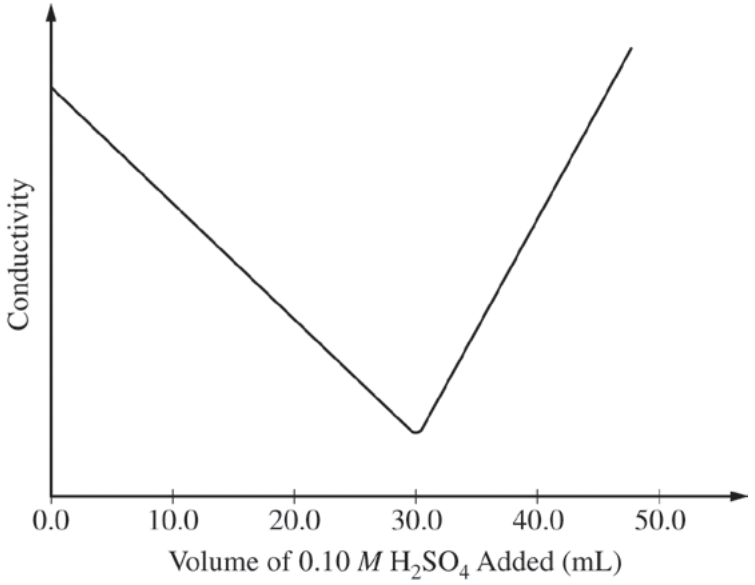
STOP

IF YOU FINISH BEFORE TIME IS CALLED, YOU MAY CHECK YOUR WORK.

DO NOT TURN TO SECTION II UNTIL YOU ARE TOLD TO DO SO

CHEMISTRY
Section II
7 Constructed-Response Questions
(Time—90 minutes)
YOU MAY USE YOUR CALCULATOR FOR SECTION II

Directions: Questions 1, 2, and 3 are long constructed-response questions that should require about 20 minutes each to answer. Questions 4, 5, 6, and 7 are short constructed-response questions that should require about seven minutes each to answer. Read each question carefully and write your response in the space provided following each question. Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Specific answers are preferable to broad, diffuse responses. For calculations, clearly show the method used and the steps involved in arriving at your answers. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not.



1. A student performs an experiment in which the conductivity of a solution of $Ba(OH)_2$ is monitored as the solution is titrated with 0.10 M H_2SO_4. The original volume of the $Ba(OH)_2$ solution is 25.0 mL. A precipitate of $BaSO_4$ ($K_{sp} = 1.0 \times 10^{-10}$) formed during the titration. The data collected from the experiment are plotted in the graph above.

   (a) As the first 30.0 mL of 0.10 M H_2SO_4 are added to the $Ba(OH)_2$ solution, two types of chemical reactions occur simultaneously. On the lines provided below, write the balanced net-ionic equations for (i) the neutralization reaction and (ii) the precipitation reaction.

   (i) Equation for neutralization reaction: _____

   (ii) Equation for precipitation reaction: _____

GO ON TO THE NEXT PAGE.

(b) The conductivity of the $Ba(OH)_2$ solution decreases as the volume of added 0.10 *M* H_2SO_4 changes from 0.0 mL to 30.0 mL.

(i) Identify the chemical species that enable the solution to conduct electricity as the first 30.0 mL of 0.10 *M* H_2SO_4 are added.

(ii) On the basis of the equations you wrote in part (a), explain why the conductivity decreases.

(c) Using the information in the graph, calculate the molarity of the original $Ba(OH)_2$ solution.

(d) Calculate the concentration of $Ba^{2+}(aq)$ in the solution at the equivalence point (after exactly 30.0 mL of 0.10 *M* H_2SO_4 are added).

(e) The concentration of $Ba^{2+}(aq)$ in the solution decreases as the volume of added 0.10 *M* H_2SO_4 increases from 30.0 mL to 31.0 mL. Explain.

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 1

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 1

GO ON TO THE NEXT PAGE.

2. A student is given the task of determining the enthalpy of reaction for the reaction between HCl(aq) and NaOH(aq). The following materials are available.

1.00 *M* HCl(aq)	1.00 *M* NaOH(aq)	distilled water
2.00 *M* HCl(aq)	2.00 *M* NaOH(aq)	goggles
insulated cups with covers	gloves	lab coat
thermometer (± 0.1°C)	stirring rod	

The student may select from the glassware listed in the table below.

Glassware Items	Precision
250 mL Erlenmeyer flasks	± 25 mL
100 mL beakers	± 10 mL
100 mL graduated cylinders	± 0.1 mL

(a) The student selects two 100 mL beakers, uses them to measure 50 mL each of 1.00 *M* HCl(aq) solution and 1.00 *M* NaOH(aq) solution, and measures an initial temperature of 24.5°C for each solution. Then the student pours the two solutions into an insulated cup, stirs the mixture, covers the cup, and records a maximum temperature of 29.9°C.

(i) Is the experimental design sufficient to determine the enthalpy of reaction to a precision of two significant figures? Justify your answer.

(ii) List two specific changes to the experiment that will allow the student to determine the enthalpy of reaction to a precision of three significant figures. Explain.

(b) A second student is given two solutions, 75.0 mL of 1.00 *M* HCl and 75.0 mL of 1.00 *M* NaOH, each at 25.0°C. The student pours the solutions into an insulated cup, stirs the mixture, covers the cup, and records the maximum temperature of the mixture.

(i) The student calculates the amount of heat evolved in the experiment to be 4.1 kJ. Calculate the student's experimental value for the enthalpy of reaction, in kJ/mol$_{rxn}$.

(ii) The student assumes that the thermometer and the calorimeter do not absorb energy during the reaction. Does this assumption result in a calculated value of the enthalpy of reaction that is higher than, lower than, or the same as it would have been had the heat capacities of the thermometer and calorimeter been taken into account? Justify your answer.

(iii) One assumption in interpreting the results of the experiment is that the reaction between HCl(aq) and NaOH(aq) goes to completion. Justify the validity of this assumption in terms of the equilibrium constant for the reaction.

(c) A third student calculates a value for the enthalpy of reaction that is significantly higher than the accepted value.

(i) Identify a specific error in procedure made by the student that will result in a calculated value for the enthalpy of reaction that is higher than the accepted value. (Vague statements like "human error" or "incorrect calculations" will not earn credit.)

(ii) Explain how the error that you identified in part (c)(i) leads to a calculated value for the enthalpy of reaction that is higher than the accepted value.

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 2

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 2

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 2

GO ON TO THE NEXT PAGE.

$$SO_2Cl_2(g) \rightleftarrows SO_2(g) + Cl_2(g)$$

3. A 4.32 g sample of liquid SO_2Cl_2 is placed in a rigid, evacuated 1.50 L reaction vessel. As the container is heated to 400. K, the sample vaporizes completely and starts to decompose according to the equation above. The decomposition reaction is endothermic.

   (a) If no decomposition occurred, what would be the pressure, in atm, of the $SO_2Cl_2(g)$ in the vessel at 400. K ?

   (b) When the system has reached equilibrium at 400. K, the total pressure in the container is 1.26 atm. Calculate the partial pressures, in atm, of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ in the container at 400. K.

   (c) For the decomposition reaction at 400. K,

      (i) write the equilibrium-constant expression for K_p for the reaction, and

      (ii) calculate the value of the equilibrium constant, K_p.

   (d) The temperature of the equilibrium mixture is increased to 425 K. Will the value of K_p increase, decrease, or remain the same? Justify your prediction.

   (e) In another experiment, the original partial pressures of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ are 1.0 atm each at 400. K. Predict whether the amount of $SO_2Cl_2(g)$ in the container will increase, decrease, or remain the same. Justify your prediction.

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 3

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 3

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 3

GO ON TO THE NEXT PAGE.

$$2\ NO_2(g)\ +\ F_2(g)\ \rightarrow\ 2\ NO_2F(g)$$

4. It is proposed that the reaction represented above proceeds via the mechanism represented by the two elementary steps shown below.

Step I: $NO_2\ +\ F_2\ \rightarrow\ NO_2F\ +\ F$ (*slow*)

Step II: $NO_2\ +\ F\ \rightleftarrows\ NO_2F$ (*fast reversible*)

(a) Step I of the proposed mechanism involves the collision between NO_2 and F_2 molecules. This step is slow even though such collisions occur very frequently in a mixture of $NO_2(g)$ and $F_2(g)$. Consider a specific collision between a molecule of NO_2 and a molecule of F_2.

(i) One factor that affects whether the collision will result in a reaction is the magnitude of the collision energy. Explain.

(ii) Identify and explain one other factor that affects whether the collision will result in a reaction.

(b) Consider the following potential rate laws for the reaction. Circle the rate law below that is consistent with the mechanism proposed above. Explain the reasoning behind your choice in terms of the details of the elementary steps of the mechanism.

rate = $k[NO_2]^2[F_2]$ rate = $k[NO_2][F_2]$

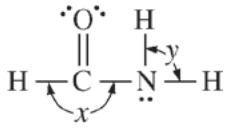
GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 4

GO ON TO THE NEXT PAGE.

5. Methanamide, CH_3NO, is a liquid at 25°C.

(a) The complete Lewis electron-dot diagram for methanamide is shown below.



(i) In the molecule, angle x is not 180°. Estimate the observed angle. Justify your answer.

(ii) In the molecule, angle y is not 90°. Explain why in terms of electron domains (VSEPR model).

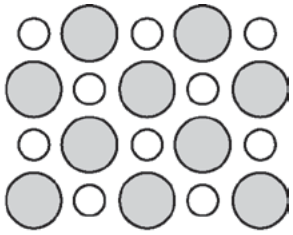
(b) Consider a molecule with the formula CH_2O_2. The structure of this molecule has a geometry around the carbon atom similar to the geometry around carbon in methanamide. In the box provided below, draw the complete Lewis electron-dot diagram for the molecule.

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 5

GO ON TO THE NEXT PAGE.

H_2O molecule

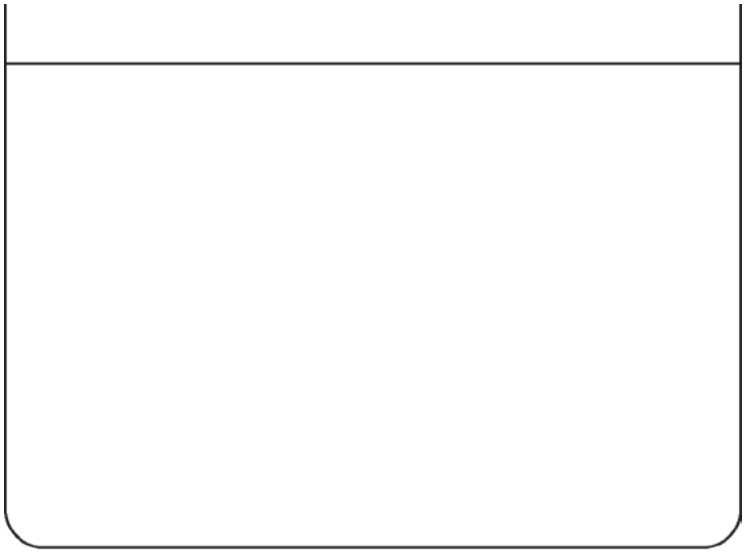


LiCl crystal

6. The structures of a water molecule and a crystal of LiCl(*s*) are represented above. A student prepares a 1.0 *M* solution by dissolving 4.2 g of LiCl(*s*) in enough water to make 100 mL of solution.

   (a) In the space provided below, show the interactions of the components of LiCl(*aq*) by making a drawing that represents the different particles present in the solution. Base the particles in your drawing on the particles shown in the representations above. Include only one formula unit of LiCl and no more than ten molecules of water. Your drawing must include the following details.

   - identity of ions (symbol and charge)
   - the arrangement and proper orientation of the particles in the solution



LiCl (*aq*)

   (b) The student passes a direct current through the solution and observes that chlorine gas is produced at the anode. Identify the chemical species produced at the cathode and justify your answer using the information given in the table below.

Half-reaction	Standard Reduction Potential at 25°C (V)
$Li^+(aq) + e^- \rightarrow Li(s)$	– 3.05
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	– 0.83

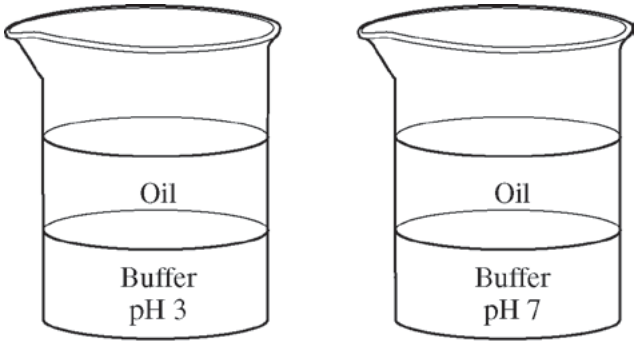
GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 6

GO ON TO THE NEXT PAGE.

$$\underset{\textit{yellow}}{HIn(aq)} + H_2O(l) \rightleftarrows \underset{\textit{blue}}{In^-(aq)} + H_3O^+(aq)$$

7. The indicator HIn is a weak acid with a pK_a value of 5.0. It reacts with water as represented in the equation above. Consider the two beakers below. Each beaker has a layer of colorless oil (a nonpolar solvent) on top of a layer of aqueous buffer solution. In beaker X the pH of the buffer solution is 3, and in beaker Y the pH of the buffer solution is 7. A small amount of HIn is placed in both beakers. The mixtures are stirred well, and the oil and water layers are allowed to separate.



Beaker X Beaker Y

(a) What is the predominant form of HIn in the aqueous buffer in beaker Y, the acid form or the conjugate base form? Explain your reasoning.

(b) In beaker X the oil layer is yellow, whereas in beaker Y the oil layer is colorless. Explain these observations in terms of both acid-base equilibria and interparticle forces.

GO ON TO THE NEXT PAGE.

ADDITIONAL PAGE FOR ANSWERING QUESTION 7

GO ON TO THE NEXT PAGE.

INFORMATION IN THE TABLE BELOW AND ON THE FOLLOWING PAGES MAY BE USEFUL IN ANSWERING THE QUESTIONS IN THIS SECTION OF THE EXAMINATION.

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1																		2
H																		**He**
1.008																		4.00
3	4											5	6	7	8	9	10	
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**	
6.94	9.01											10.81	12.01	14.01	16.00	19.00	20.18	
11	12											13	14	15	16	17	18	
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**	
22.99	24.30											26.98	28.09	30.97	32.06	35.45	39.95	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**	
39.10	40.08	44.96	47.90	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.39	69.72	72.59	74.92	78.96	79.90	83.80	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**	
85.47	87.62	88.91	91.22	92.91	95.94	(98)	101.1	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.91	131.29	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs	**Ba**	***La**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**	
132.91	137.33	138.91	178.49	180.95	183.85	186.21	190.2	192.2	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)	
87	88	89	104	105	106	107	108	109	110	111								
Fr	**Ra**	**†Ac**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**								
(223)	226.02	227.03	(261)	(262)	(266)	(264)	(277)	(268)	(271)	(272)								

	58	59	60	61	62	63	64	65	66	67	68	69	70	71
*Lanthanide Series	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	140.12	140.91	144.24	(145)	150.4	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
	90	91	92	93	94	95	96	97	98	99	100	101	102	103
†Actinide Series	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the test 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

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

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

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

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

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

$= K_a \times K_b$

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

$14 = pH + pOH$

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

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

Equilibrium Constants

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

KINETICS

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

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

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

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

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

$$\text{K} = \text{°C} + 273$$

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

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

$$\text{Molarity, } M = \text{moles of solute per liter of solution}$$

$$A = abc$$

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, $R = 8.314 \text{ J mol}^{-1}\text{ K}^{-1}$
$= 0.08206 \text{ L atm mol}^{-1}\text{ K}^{-1}$
$= 62.36 \text{ L torr mol}^{-1}\text{ K}^{-1}$
$1 \text{ atm} = 760 \text{ mm Hg}$
$= 760 \text{ torr}$
STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT \ln K$$
$$= -n F E^\circ$$

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

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

Faraday's constant, F = 96,485 coulombs per mole of electrons
$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$

APPENDIX - ANSWERS

AP CHEMISTRY 2013

Multiple-choice key transcribed from the matching supplied source.

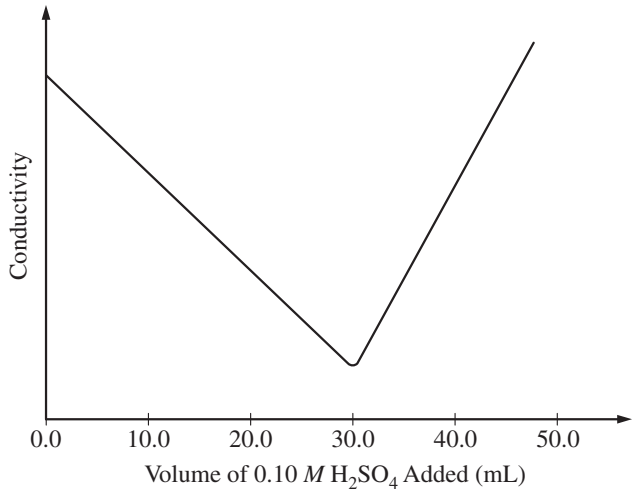
Question	Answer	Question	Answer	Question	Answer
1	C	21	A	41	C
2	C	22	D	42	C
3	A	23	D	43	D
4	A	24	D	44	C
5	D	25	C	45	B
6	D	26	B	46	C
7	B	27	D	47	C
8	D	28	C	48	A
9	B	29	C	49	B
10	C	30	C	50	C
11	B	31	B	51	D
12	B	32	B	52	C
13	C	33	B	53	A
14	A	34	C	54	A
15	B	35	C	55	C
16	C	36	B	56	D
17	B	37	A	57	B
18	D	38	C	58	B
19	B	39	A	59	B
20	C	40	A	60	B

Practice paper effective Fall 2013, previewing the revised 2014 format.

Matching original FRQ scoring material follows in this appendix.

Scoring Guidelines for Free-Response Question 1

Question 1
(10 Points)



A student performs an experiment in which the conductivity of a solution of $Ba(OH)_2$ is monitored as the solution is titrated with 0.10 *M* H_2SO_4. The original volume of the $Ba(OH)_2$ solution is 25.0 mL. A precipitate of $BaSO_4$ ($K_{sp} = 1.0 \times 10^{-10}$) formed during the titration. The data collected from the experiment are plotted in the graph above.

(a) As the first 30.0 mL of 0.10 *M* H_2SO_4 are added to the $Ba(OH)_2$ solution, two types of chemical reactions occur simultaneously. On the lines provided below, write the balanced net-ionic equations for (i) the neutralization reaction and (ii) the precipitation reaction.

(i) Equation for neutralization reaction: _____

(ii) Equation for precipitation reaction: _____

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	1 point is earned for <u>each</u> correct product. 1 point is earned for the correct reactants with atoms <u>and</u> charges balanced in <u>both</u> reactions.

(b) The conductivity of the $Ba(OH)_2$ solution decreases as the volume of added 0.10 *M* H_2SO_4 changes from 0.0 mL to 30.0 mL.

(i) Identify the chemical species that enable the solution to conduct electricity as the first 30.0 mL of 0.10 *M* H_2SO_4 are added.

$Ba^{2+}(aq)$ and/or $OH^-(aq)$	1 point is earned for either ion.

(ii) On the basis of the equations you wrote in part (a), explain why the conductivity decreases.

As the titration approaches the equivalence point, $Ba^{2+}(aq)$ ions are removed from solution by the precipitation reaction, <u>and</u> $OH^-(aq)$ ions are removed from solution by the neutralization reaction.	1 point is earned for each correct explanation. <u>Note</u>: response must refer to <u>both</u> reactions for full credit.

(c) Using the information in the graph, calculate the molarity of the original $Ba(OH)_2$ solution.

moles $Ba(OH)_2$ = moles H_2SO_4 (at equivalence point) moles $H_2SO_4 = \frac{0.10\ \text{mol}}{1.0\ \text{L}} \times 0.030\ \text{L} = 0.0030\ \text{mol}$ $[Ba(OH)_2] = \frac{\text{mol } Ba(OH)_2}{\text{volume of original solution}} =$ $\frac{0.0030\ \text{mol}}{0.025\ \text{L}} = 0.12\ M$	1 point is earned for the correct determination of the number of moles of titrant added at the equivalence point (can be implicit). 1 point is earned for the correct calculation of the original concentration of $Ba(OH)_2(aq)$.

(d) Calculate the concentration of $Ba^{2+}(aq)$ in the solution at the equivalence point (after exactly 30.0 mL of 0.10 *M* H_2SO_4 are added).

$K_{sp} = [Ba^{2+}] \times [SO_4^{2-}] = 1.0 \times 10^{-10}$ $[Ba^{2+}] = [SO_4^{2-}]$ $[Ba^{2+}] = \sqrt{1.0 \times 10^{-10}} = 1.0 \times 10^{-5}\ M$	1 point is earned for the correct calculation based on K_{sp}.

(e) The concentration of $Ba^{2+}(aq)$ in the solution decreases as the volume of added 0.10 *M* H_2SO_4 increases from 30.0 mL to 31.0 mL. Explain.

Because of the common ion effect, adding sulfate ions to an equilibrium reaction involving sulfate ions will cause the reaction to consume the added ions as a new equilibrium is established. Consequently, more $BaSO_4(s)$ is formed, causing the $Ba^{2+}(aq)$ concentration to decrease.	1 point is earned for a correct explanation, which must use an equilibrium argument (for example, citing the common ion effect or Le Chatelier's principle) rather than a stoichiometric argument.

Scoring Guidelines for Free-Response Question 2

Question 2
(10 Points)

A student is given the task of determining the enthalpy of reaction for the reaction between HCl(*aq*) and NaOH(*aq*). The following materials are available.

1.00 *M* HCl(*aq*)	1.00 *M* NaOH(*aq*)	distilled water
2.00 *M* HCl(*aq*)	2.00 *M* NaOH(*aq*)	goggles
insulated cups with covers	gloves	lab coat
thermometer (± 0.1°C)	stirring rod	

The student may select from the glassware listed in the table below.

Glassware Items	Precision
250 mL Erlenmeyer flasks	± 25 mL
100 mL beakers	± 10 mL
100 mL graduated cylinders	± 0.1 mL

(a) The student selects two 100 mL beakers, uses them to measure 50 mL each of 1.00 *M* HCl(*aq*) solution and 1.00 *M* NaOH(*aq*) solution, and measures an initial temperature of 24.5°C for each solution. Then the student pours the two solutions into an insulated cup, stirs the mixture, covers the cup, and records a maximum temperature of 29.9°C.

(i) Is the experimental design sufficient to determine the enthalpy of reaction to a precision of two significant figures? Justify your answer.

No. The use of the beakers to measure 50 mL ±10 mL of solutions limits the precision of the volume measurements and of the calculations to ±20% or 1 significant figure.	1 point is earned for the correct answer with the correct explanation.

(ii) List two specific changes to the experiment that will allow the student to determine the enthalpy of reaction to a precision of three significant figures. Explain.

Use graduated cylinders to measure the volumes of acid and base allowing a volume precision of ±0.1 mL or 3 significant figures for a volume of 50.0 mL. AND Use the 2.00 *M* HCl and 2.00 *M* NaOH solutions (instead of 1.00 *M*) to get a larger ΔT, thereby improving the relative precision in ΔT to ±1%.	1 point is earned for the change of glassware to graduated cylinders with a proper explanation. 1 point is earned for using the 2.00 *M* solutions for improved relative precision in temperature. Note: doubling the volumes will not increase ΔT or significantly improve volume precision.

(b) A second student is given two solutions, 75.0 mL of 1.00 *M* HCl and 75.0 mL of 1.00 *M* NaOH, each at 25.0°C. The student pours the solutions into an insulated cup, stirs the mixture, covers the cup, and records the maximum temperature of the mixture.

(i) The student calculates the amount of heat evolved in the experiment to be 4.1 kJ. Calculate the student's experimental value for the enthalpy of reaction, in kJ/mol$_{rxn}$.

$75.0 \text{ mL} \times \frac{1.00 \text{ mol HCl (or NaOH)}}{1000 \text{ mL}} = 0.0750 \text{ mol HCl (or NaOH)}$ $\Delta H = \frac{-4.1 \text{ kJ}}{0.0750 \text{ mol of reactants}} = -55 \text{ kJ/mol}_{rxn}$	1 point is earned for the correct calculation of moles of reactants. 1 point is earned for the correct substitution and answer.

(ii) The student assumes that the thermometer and the calorimeter do not absorb energy during the reaction. Does this assumption result in a calculated value of the enthalpy of reaction that is higher than, lower than, or the same as it would have been had the heat capacities of the thermometer and calorimeter been taken into account? Justify your answer.

The calculated value of the enthalpy of reaction will be <u>lower</u> (smaller or less negative) than it would have been had the thermometer and calorimeter been taken into account. The thermometer and calorimeter will absorb some of the heat of reaction. This lost heat is ignored in the original calculation of ΔH_{rxn}, making it smaller in magnitude (less negative).	1 point is earned for the correct prediction.
OR The actual heat capacity of the system is the sum of the heat capacities of the water, thermometer, and calorimeter. The assumed heat capacity of the system (water only) is less than the actual value, resulting in a lower (less negative) calculated value of ΔH_{rxn}.	1 point is earned for an acceptable justification.

(iii) One assumption in interpreting the results of the experiment is that the reaction between HCl(*aq*) and NaOH(*aq*) goes to completion. Justify the validity of this assumption in terms of the equilibrium constant for the reaction.

$H^+ + OH^- \rightarrow H_2O$, the reaction between HCl(*aq*) and NaOH(*aq*), is the <u>reverse</u> of $H_2O \rightarrow H^+ + OH^-$, the autoionization of water (for which $K = K_w = 1.0 \times 10^{-14}$). Thus the value of K for the neutralization reaction is the reciprocal of K_w, or 1.0×10^{14}, a very large number. Thus the neutralization reaction goes virtually to completion.	1 point is earned for the correct justification.

(c) A third student calculates a value for the enthalpy of reaction that is significantly higher than the accepted value.

(i) Identify a specific error in procedure made by the student that will result in a calculated value for the enthalpy of reaction that is higher than the accepted value. (Vague statements like "human error" or "incorrect calculations" will not earn credit.)

The student read the thermometer incorrectly in such a way to result in a calculated value of ΔT that was too high (either read T_i too low or read T_f too high). OR The student mistakenly used 2.00 *M* acid and 2.00 *M* base, thinking they were both 1.00 *M*.	1 point is earned for an acceptable procedural error that results in a higher calculated value.

(ii) Explain how the error that you identified in part (c)(i) leads to a calculated value for the enthalpy of reaction that is higher than the accepted value.

The calculation of the molar enthalpy of reaction may be expressed as Molar $\Delta H_{rxn} = -\dfrac{\text{mass}_{soln} \times c \times \Delta T}{n_{rxn}}$. If there is a measurement error that results in a ΔT that is too high, the magnitude (i.e., the absolute value) of the calculated molar enthalpy of reaction will be too high.	1 point is earned for an explanation that is consistent with the stated procedural error.

Question 3
(10 Points)

$$SO_2Cl_2(g) \rightleftarrows SO_2(g) + Cl_2(g)$$

A 4.32 g sample of liquid SO_2Cl_2 is placed in a rigid, evacuated 1.50 L reaction vessel. As the container is heated to 400. K, the sample vaporizes completely and starts to decompose according to the equation above. The decomposition reaction is endothermic.

(a) If no decomposition occurred, what would be the pressure, in atm, of the $SO_2Cl_2(g)$ in the vessel at 400. K ?

Assuming no decomposition, $\text{moles}_{SO_2Cl_2} = \frac{m}{M} = \frac{4.32\text{ g}}{134.96\text{ g/mol}} = 0.0320\text{ mol}$ $p_{SO_2Cl_2} = \frac{nRT}{V} = \frac{(0.0320\text{ mol})(0.0821\text{ L·atm/mol·K})(400.\text{ K})}{1.50\text{ L}}$ $= 0.701\text{ atm}$	1 point is earned for the correct calculation of moles of SO_2Cl_2 (may be implicit). 1 point is earned for the correct calculation of the pressure.

(b) When the system has reached equilibrium at 400. K, the total pressure in the container is 1.26 atm. Calculate the partial pressures, in atm, of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ in the container at 400. K.

Pressures at equilibrium at 400. K: $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ Total $0.701 - x \quad x \quad x \quad 0.701 + x$ $p_{total} = 0.701 + x = 1.26$ atm $x = p_{SO_2} = p_{Cl_2} = 0.56$ atm $p_{SO_2Cl_2} = 0.701 - x = 0.14$ atm	1 point is earned for the correct setup. 1 point is earned for the correct calculation of pressures.

(c) For the decomposition reaction at 400. K,

(i) write the equilibrium-constant expression for K_p for the reaction, and

$K_p = \frac{p_{SO_2} \cdot p_{Cl_2}}{p_{SO_2Cl_2}}$	1 point is earned for the correct K_p expression. Note: the pressure subscripts must be specific (i.e., SO_2, Cl_2, and SO_2Cl_2 — NOT, e.g., A, B, C, and D).

(ii) calculate the value of the equilibrium constant, K_p.

$K_p = \frac{(0.56)(0.56)}{0.14} = 2.2$	1 point is earned for the correct calculation of K_p that is consistent with the K_p expression stated in part (c)(i) and with the partial pressures calculated in part (b).

(d) The temperature of the equilibrium mixture is increased to 425 K. Will the value of K_p increase, decrease, or remain the same? Justify your prediction.

At a higher temperature, K_p will increase. According to Le Chatelier's principle, raising the temperature of an endothermic reaction at equilibrium adds a thermal stress that increases the value of K_p and produces more products.	1 point is earned for the correct prediction. 1 point is earned for a proper justification in terms of Le Chatelier's principle.

(e) In another experiment, the original partial pressures of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ are 1.0 atm each at 400. K. Predict whether the amount of $SO_2Cl_2(g)$ in the container will increase, decrease, or remain the same. Justify your prediction.

The amount of SO_2Cl_2 in the container will decrease. Initially $Q_p = 1.0 < 2.2. = K_p$, thus the reaction will consume SO_2Cl_2 as it proceeds in the forward direction to reestablish equilibrium.	1 point is earned for the correct prediction. 1 point is earned for an acceptable justification. Note: the justification must consider the relative values of Q_p and K_p.

Question 4
(4 Points)

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

It is proposed that the reaction represented above proceeds via the mechanism represented by the two elementary steps shown below.

Step I: $NO_2 + F_2 \rightarrow NO_2F + F$ *(slow)*

Step II: $NO_2 + F \rightleftarrows NO_2F$ *(fast reversible)*

(a) Step I of the proposed mechanism involves the collision between NO_2 and F_2 molecules. This step is slow even though such collisions occur very frequently in a mixture of $NO_2(g)$ and $F_2(g)$. Consider a specific collision between a molecule of NO_2 and a molecule of F_2.

(i) One factor that affects whether the collision will result in a reaction is the magnitude of the collision energy. Explain.

Successful molecular collisions must have sufficient energy in order to result in reaction. Only collisions with sufficient energy to overcome the activation energy barrier, E_a, will be able to reach the transition state and begin to break the F–F bond.	1 point is earned for a correct explanation that makes reference to the activation energy of the reaction.

(ii) Identify and explain one other factor that affects whether the collision will result in a reaction.

For a collision to be successful, the molecules must have the correct orientation. Only collisions with the correct orientation will be able to begin to form an N–F bond and begin to break an F–F bond as the transition state is approached (that is, the molecules must contact each other at very specific locations on their surfaces for the transition state to be accessible).	1 point is earned for identifying the relative orientation of the colliding molecules. 1 point is earned for an explanation that makes reference to specific parts (atoms or bonds) of the reacting molecules.

(b) Consider the following potential rate laws for the reaction. Circle the rate law below that is consistent with the mechanism proposed above. Explain the reasoning behind your choice in terms of the details of the elementary steps of the mechanism.

$\text{rate} = k[NO_2]^2[F_2]$ $\text{rate} = k[NO_2][F_2]$

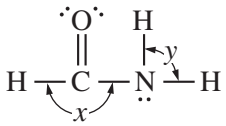
The rate law that is consistent with the mechanism is the one on the right above (rate = $k[NO_2][F_2]$). Step I is the slower step and the rate-determining step in the mechanism. Since Step I is an elementary reaction, its rate law is given by the stoichiometry of the reacting molecules, $\text{rate}_{\text{Step I}} = k_1[NO_2][F_2]$.	1 point is earned for identifying the correct rate law with a proper explanation. The explanation must correlate the overall rate law with the rate law derived from the stoichiometry of the slow step in the mechanism. Note: a statement relating the coefficients of the reactants in Step I to the exponents in the rate law indicates a correct understanding.

Scoring Guidelines for Question 5

Question 5
(4 Points)

Methanamide, CH_3NO, is a liquid at 25°C.

(a) The complete Lewis electron-dot diagram for methanamide is shown below.



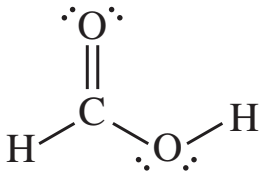
(i) In the molecule, angle *x* is not 180°. Estimate the observed angle. Justify your answer.

Angle *x* is approximately 120°. Three electron domains around the carbon atom will maximally separate the electrons and minimize the energy when the bond angles are 120°.	1 point is earned for the correct angle with justification. Note: accept 120° ± 10° for the angle (i.e., 110° ≤ *x* ≤ 130°.) Also accept steric number (SN) = 3 or trigonal planar geometry for the justification in part (i) only.)

(ii) In the molecule, angle *y* is not 90°. Explain why in terms of electron domains (VSEPR model).

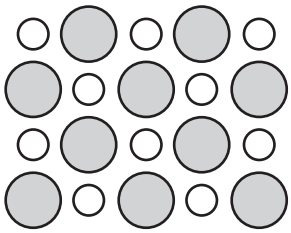
Angle *y* is approximately 109.5°. Four electron domains around the nitrogen atom will maximally separate the electrons and minimize the energy when the bond angles are 109.5°. OR Angle *y* is approximately 120°. Considering possible resonance structures involving a double bond between the C and N atoms, there are three electron domains around the nitrogen atom. In this case, minimization of energy leads to bond angles of approximately 120°.	1 point is earned for the correct justification for an angle different than 90°. Note: the justification need not give a specific bond angle, but it must mention the repulsion of 4 electron domains (or 3 electron domains, if resonance structures are mentioned).

(b) Consider a molecule with the formula CH_2O_2. The structure of this molecule has a geometry around the carbon atom similar to the geometry around carbon in methanamide. In the box provided below, draw the complete Lewis electron-dot diagram for the molecule.

	2 points are earned for a correct Lewis electron-dot diagram for formic acid. Notes: 1 point is earned for the correct skeletal structure for formic acid with the C=O double bond (i.e., containing all five bonding pairs) but missing one or more lone pairs. Also, 1 point is earned for a Lewis electron-dot diagram representing (i) the correct molecular formula (CH_2O_2) (ii) with three electron domains and at least three bonded pairs of electrons around the carbon atom, with no more than three bonded pairs of electrons around any oxygen atom, and (iii) the proper distribution of all 18 electrons in accordance with the octet rule.

Question 6
(4 Points)

H_2O molecule

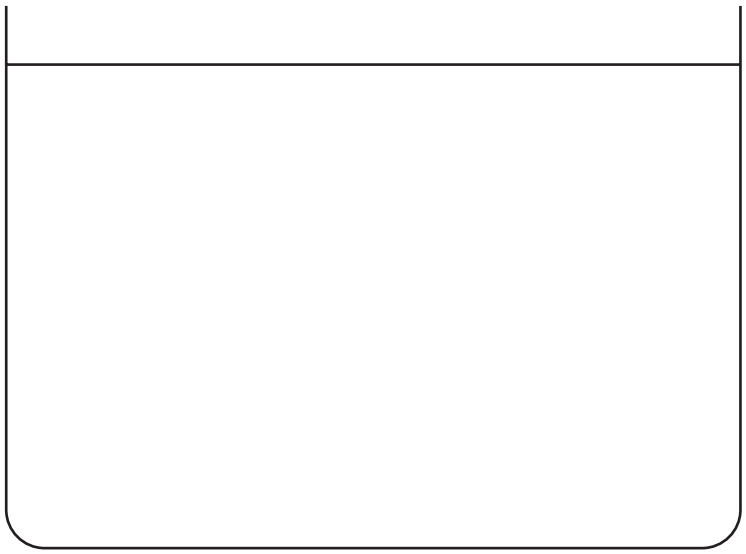


LiCl crystal

The structures of a water molecule and a crystal of LiCl(*s*) are represented above. A student prepares a 1.0 *M* solution by dissolving 4.2 g of LiCl(*s*) in enough water to make 100 mL of solution.

(a) In the space provided below, show the interactions of the components of LiCl(*aq*) by making a drawing that represents the different particles present in the solution. Base the particles in your drawing on the particles shown in the representations above. Include only one formula unit of LiCl and no more than ten molecules of water. Your drawing must include the following details.

- identity of ions (symbol and charge)
- the arrangement and proper orientation of the particles in the solution



LiCl (*aq*)

The sketch should clearly show: 1. a clear representation of at least one Li^+ ion and one Cl^- ion separated from each other, labeled, and charged; 2. each ion surrounded by at least two H_2O molecules; and 3. H_2O molecules with the proper orientation around each ion (i.e., the oxygen end of the water molecules closer to the lithium ion and the hydrogen end of the water molecules closer to the chloride ion).	1 point is earned for a correctly drawn and labeled particulate representation of the ions. (Representation must indicate that the smaller ion is Li^+. Representations that include more than one formula unit of LiCl (dissolved or undissolved) are acceptable as long as at least one of the formula units is separated into its ions and the ions are correctly labeled with their respective identities and charges.) 1 point is earned for a correctly drawn particulate representation of water molecules of hydration surrounding the ions. 1 point is earned for correctly representing the orientation of the water molecules of hydration with the proper polarity.

(b) The student passes a direct current through the solution and observes that chlorine gas is produced at the anode. Identify the chemical species produced at the cathode and justify your answer using the information given in the table below.

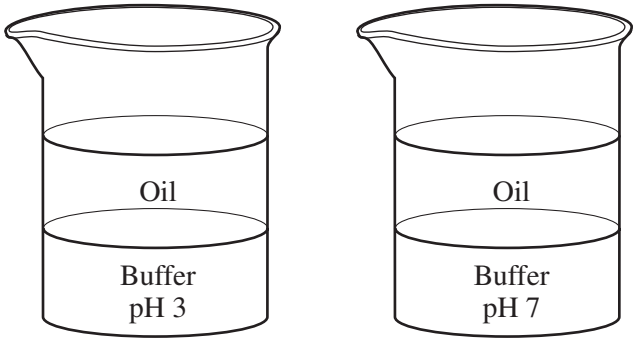
Half-reaction	Standard Reduction Potential at 25°C (V)
$Li^+(aq) + e^- \rightarrow Li(s)$	− 3.05
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	− 0.83

$H_2(g)$ and $OH^-(aq)$ The hydrogen atoms in H_2O are reduced to H_2 at the cathode because this reaction has a higher (more favorable or less negative) standard reduction potential than the reduction of lithium ions to $Li(s)$.	1 point is earned for correctly identifying either of the chemical species produced at the cathode with the proper justification. Note: the justification must clearly indicate that "higher" means "less negative." A "lower magnitude" negative value also earns the point.

Question 7
(4 Points)

$$\underset{\textit{yellow}}{HIn(aq)} + H_2O(l) \rightleftarrows \underset{\textit{blue}}{In^-(aq)} + H_3O^+(aq)$$

The indicator HIn is a weak acid with a pK_a value of 5.0. It reacts with water as represented in the equation above. Consider the two beakers below. Each beaker has a layer of colorless oil (a nonpolar solvent) on top of a layer of aqueous buffer solution. In beaker X the pH of the buffer solution is 3, and in beaker Y the pH of the buffer solution is 7. A small amount of HIn is placed in both beakers. The mixtures are stirred well, and the oil and water layers are allowed to separate.



Beaker X Beaker Y

(a) What is the predominant form of HIn in the aqueous buffer in beaker Y, the acid form or the conjugate base form? Explain your reasoning.

The conjugate base form, $In^-(aq)$, is the predominant form of the indicator in the aqueous pH 7 buffer in beaker Y. This is because the pH is greater than the pK_a of HIn, causing the equilibrium to form a significant amount of products, $In^-(aq)$ and $H_3O^+(aq)$.	1 point is earned for correctly identifying $In^-(aq)$ as the predominant form in the aqueous layer of beaker Y because the solution is not acidic (may be implicit). 1 point is earned for stating that pH > pK_a and that this causes the equilibrium to favor the products.

(b) In beaker X the oil layer is yellow, whereas in beaker Y the oil layer is colorless. Explain these observations in terms of both acid-base equilibria and interparticle forces.

At pH 3 the acid form $HIn(aq)$ predominates in the aqueous layer of beaker X because pH < pK_a. Since $HIn(aq)$ is a neutral molecule, some of it can dissolve in the oil layer of beaker X because of London dispersion interactions with the oil, causing the oil layer to be yellow. Since $In^-(aq)$ is charged, it will preferentially dissolve in the aqueous layer of beaker Y because of ion-dipole interactions with the water, leaving the oil layer colorless.	1 point is earned for explaining the yellow color in the oil layer of beaker X in terms of acid-base equilibrium and interparticle forces between HIn molecules and oil molecules. 1 point is earned for explaining the colorless oil layer of beaker Y in terms of interparticle forces between In^- ions and water molecules.