RELEASED EXAM

1999

AP® Chemistry

CONTAINS:

- Multiple-Choice Questions and Answer Key
- Free-Response Questions, Scoring Guidelines, and Sample Student Responses with Commentary
- Statistical Information about Student Performance on the 1999 Exam

Advanced Placement Program®

The College Board
Educational Excellence for All Students

CHEMISTRY

Three hours are allotted for this examination. One hour and 30 minutes are allotted for Section I, which consists of multiple-choice questions. For Section II, Part A, 40 minutes are allotted; for Section II, Part B, 50 minutes are allotted. Section I is printed in this examination booklet. Section II is printed in a separate booklet.

NO CALCULATORS MAY BE USED IN THIS SECTION OF THE EXAMINATION.

SECTION I

Time — 1 hour and 30 minutes
Number of questions — 75
Percent of total grade — 45

This examination contains 75 multiple-choice questions and 5 survey questions. Therefore, please be careful to fill in only the ovals that are preceded by numbers 1 through 80 on your answer sheet. NO CALCULATORS ARE ALLOWED.

General Instructions

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE INSTRUCTED TO DO SO.

INDICATE ALL YOUR ANSWERS TO QUESTIONS IN SECTION I ON THE SEPARATE ANSWER SHEET. No credit will be given for anything written in this examination booklet, but you may use the booklet for notes or scratchwork. After you have decided which of the suggested answers is best, COMPLETELY fill in the corresponding oval on the answer sheet. Give only one answer to each question. If you change an answer, be sure that the previous mark is erased completely.

Example:

Chicago is a

(A) state
(B) city
(C) country
(D) continent
(E) village

Sample Answer

Ⓐ ● Ⓒ Ⓓ Ⓔ

Many candidates wonder whether or not to guess the answers to questions about which they are not certain. In this section of the examination, as a correction for haphazard guessing, one-fourth of the number of questions you answer incorrectly will be subtracted from the number of questions you answer correctly. It is improbable, therefore, that mere guessing will improve your score significantly; it may even lower your score, and it does take time. If, however, you are not sure of the correct answer but have some knowledge of the question and are able to eliminate one or more of the answer choices as wrong, your chance of getting the right answer is improved, and it may be to your advantage to answer such a question.

Use your time effectively, working as rapidly as you can without losing accuracy. Do not spend too much time on questions that are too difficult. Go on to other questions and come back to the difficult ones later if you have time. It is not expected that everyone will be able to answer all the multiple-choice questions.

MATERIAL IN THE FOLLOWING TABLE MAY BE USEFUL IN ANSWERING THE QUESTIONS IN THIS SECTION OF THE EXAMINATION.

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.179
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.938	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	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** 95.94	43 **Tc** (98)	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** 121.75	52 **Te** 127.60	53 **I** 126.91	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** 183.85	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** 226.02	89 **†Ac** 227.03	104 **Unq** (261)	105 **Unp** (262)	106 **Unh** (263)	107 **Uns** (262)	108 **Uno** (265)	109 **Une** (266)									

*Lanthanide 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** 173.04	71 **Lu** 174.97
†Actinide Series:	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	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** (260)

GO ON TO THE NEXT PAGE

CHEMISTRY

SECTION I

Time — 1 hour and 30 minutes

NO CALCULATORS MAY BE USED WITH 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.

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

T = temperature
P = pressure
V = volume
S = entropy
H = enthalpy
G = free energy
R = molar gas constant
n = number of moles

M = molar
m = molal
L, mL = liter(s), milliliter(s)
g = gram(s)
nm = nanometer(s)
atm = atmosphere(s)
J, kJ = joule(s), kilojoule(s)
V = volt(s)
mol = mole(s)

Part A

Directions: Each set of lettered choices below refers to the numbered statements immediately following it. Select the one lettered choice that best fits each statement and then fill in the corresponding oval on the answer sheet. A choice may be used once, more than once, or not at all in each set.

Questions 1-4 refer to the following types of energy.

(A) Activation energy
(B) Free energy
(C) Ionization energy
(D) Kinetic energy
(E) Lattice energy

1. The energy required to convert a ground-state atom in the gas phase to a gaseous positive ion

2. The energy change that occurs in the conversion of an ionic solid to widely separated gaseous ions

3. The energy in a chemical or physical change that is available to do useful work

4. The energy required to form the transition state in a chemical reaction

GO ON TO THE NEXT PAGE

Questions 5-8 refer to atoms for which the occupied atomic orbitals are shown below.

(A) $1s\underline{\qquad}\ 2s\underline{\ \uparrow\ }$

(B) $1s\underline{\ \uparrow\downarrow\ }\ 2s\underline{\ \uparrow\downarrow\ }$

(C) $1s\underline{\ \uparrow\downarrow\ }\ 2s\underline{\ \uparrow\downarrow\ }\ 2p\underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\qquad}$

(D) $1s\underline{\ \uparrow\downarrow\ }\ 2s\underline{\ \uparrow\downarrow\ }\ 2p\underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\downarrow\ }$

(E) $[\mathrm{Ar}]\ 4s\underline{\ \uparrow\downarrow\ }\ 3d\underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$

5. Represents an atom that is chemically unreactive

6. Represents an atom in an excited state

7. Represents an atom that has four valence electrons

8. Represents an atom of a transition metal

Questions 9-12 refer to aqueous solutions containing 1:1 mole ratios of the following pairs of substances. Assume all concentrations are 1 *M*.

(A) NH_3 and NH_4Cl

(B) H_3PO_4 and NaH_2PO_4

(C) HCl and NaCl

(D) NaOH and NH_3

(E) NH_3 and $HC_2H_3O_2$ (acetic acid)

9. The solution with the lowest pH

10. The most nearly neutral solution

11. A buffer at a pH > 8

12. A buffer at a pH < 6

GO ON TO THE NEXT PAGE

Questions 13-16 refer to the following descriptions of bonding in different types of solids.

(A) Lattice of positive and negative ions held together by electrostatic forces
(B) Closely packed lattice with delocalized electrons throughout
(C) Strong single covalent bonds with weak intermolecular forces
(D) Strong multiple covalent bonds (including π-bonds) with weak intermolecular forces
(E) Macromolecules held together with strong polar bonds

13. Cesium chloride, CsCl(*s*)

14. Gold, Au(*s*)

15. Carbon dioxide, $CO_2(s)$

16. Methane, $CH_4(s)$

Questions 17-18 refer to the following elements.

(A) Lithium
(B) Nickel
(C) Bromine
(D) Uranium
(E) Fluorine

17. Is a gas in its standard state at 298 K

18. Reacts with water to form a strong base

GO ON TO THE NEXT PAGE

Part B

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

19. Which of the following best describes the role of the spark from the spark plug in an automobile engine?

(A) The spark decreases the energy of activation for the slow step.
(B) The spark increases the concentration of the volatile reactant.
(C) The spark supplies some of the energy of activation for the combustion reaction.
(D) The spark provides a more favorable activated complex for the combustion reaction.
(E) The spark provides the heat of vaporization for the volatile hydrocarbon.

20. What mass of Au is produced when 0.0500 mol of Au_2S_3 is reduced completely with excess H_2 ?

(A) 9.85 g
(B) 19.7 g
(C) 24.5 g
(D) 39.4 g
(E) 48.9 g

21. When a solution of sodium chloride is vaporized in a flame, the color of the flame is

(A) blue
(B) yellow
(C) green
(D) violet
(E) white

22. Of the following reactions, which involves the largest decrease in entropy?

(A) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(B) $2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$

(C) $Pb(NO_3)_2(s) + 2\ KI(s) \rightarrow PbI_2(s) + 2\ KNO_3(s)$

(D) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$

(E) $4\ La(s) + 3\ O_2(g) \rightarrow 2\ La_2O_3(s)$

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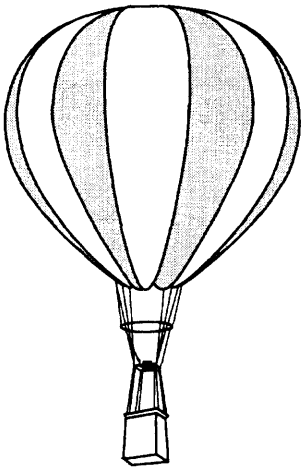


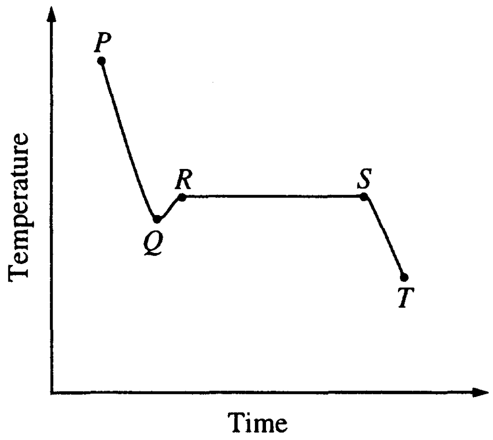
23. A hot-air balloon, shown above, rises. Which of the following is the best explanation for this observation?

(A) The pressure on the walls of the balloon increases with increasing temperature.
(B) The difference in temperature between the air inside and outside the balloon produces convection currents.
(C) The cooler air outside the balloon pushes in on the walls of the balloon.
(D) The rate of diffusion of cooler air is less than that of warmer air.
(E) The air density inside the balloon is less than that of the surrounding air.

24. The safest and most effective emergency procedure to treat an acid splash on skin is to do which of the following immediately?

(A) Dry the affected area with paper towels
(B) Sprinkle the affected area with powdered $Na_2SO_4(s)$
(C) Flush the affected area with water and then with a dilute NaOH solution
(D) Flush the affected area with water and then with a dilute $NaHCO_3$ solution
(E) Flush the affected area with water and then with a dilute vinegar solution

GO ON TO THE NEXT PAGE



25. The cooling curve for a pure substance as it changes from a liquid to a solid is shown above. The solid and the liquid coexist at

(A) point *Q* only
(B) point *R* only
(C) all points on the curve between *Q* and *S*
(D) all points on the curve between *R* and *T*
(E) no point on the curve

$$\ldots C_{10}H_{12}O_4S(s) + \ldots O_2(g) \rightarrow \ldots CO_2(g) + \ldots SO_2(g) + \ldots H_2O(g)$$

26. When the equation above is balanced and all coefficients are reduced to their lowest whole-number terms, the coefficient for $O_2(g)$ is

(A) 6
(B) 7
(C) 12
(D) 14
(E) 28

27. Appropriate uses of a visible-light spectrophotometer include which of the following?

I. Determining the concentration of a solution of $Cu(NO_3)_2$
II. Measuring the conductivity of a solution of $KMnO_4$
III. Determining which ions are present in a solution that may contain Na^+, Mg^{2+}, Al^{3+}

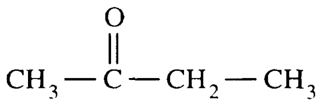
(A) I only
(B) II only
(C) III only
(D) I and II only
(E) I and III only

GO ON TO THE NEXT PAGE

28. The melting point of MgO is higher than that of NaF. Explanations for this observation include which of the following?

I. Mg^{2+} is more positively charged than Na^{+}.
II. O^{2-} is more negatively charged than F^{-}.
III. The O^{2-} ion is smaller than the F^{-} ion.

(A) II only
(B) I and II only
(C) I and III only
(D) II and III only
(E) I, II, and III



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

29. The organic compound represented above is an example of

(A) an organic acid
(B) an alcohol
(C) an ether
(D) an aldehyde
(E) a ketone

$$H_2Se(g) + 4\ O_2F_2(g) \rightarrow SeF_6(g) + 2\ HF(g) + 4\ O_2(g)$$

30. Which of the following is true regarding the reaction represented above?

(A) The oxidation number of O does not change.
(B) The oxidation number of H changes from -1 to $+1$.
(C) The oxidation number of F changes from $+1$ to -1.
(D) The oxidation number of Se changes from -2 to $+6$.
(E) It is a disproportionation reaction for F.

31. If the temperature of an aqueous solution of NaCl is increased from 20°C to 90°C, which of the following statements is true?

(A) The density of the solution remains unchanged.
(B) The molarity of the solution remains unchanged.
(C) The molality of the solution remains unchanged.
(D) The mole fraction of solute decreases.
(E) The mole fraction of solute increases.

GO ON TO THE NEXT PAGE

32. Types of hybridization exhibited by the C atoms in propene, CH_3CHCH_2, include which of the following?

I. *sp*
II. sp^2
III. sp^3

(A) I only
(B) III only
(C) I and II only
(D) II and III only
(E) I, II, and III

33. A 1.0 L sample of an aqueous solution contains 0.10 mol of NaCl and 0.10 mol of $CaCl_2$. What is the minimum number of moles of $AgNO_3$ that must be added to the solution in order to precipitate all of the Cl^- as AgCl(*s*) ? (Assume that AgCl is insoluble.)

(A) 0.10 mol
(B) 0.20 mol
(C) 0.30 mol
(D) 0.40 mol
(E) 0.60 mol

Questions 34-35 refer to an electrolytic cell that involves the following half-reaction.

$$AlF_6^{3-} + 3\,e^- \rightarrow Al + 6\,F^-$$

34. Which of the following occurs in the reaction?

(A) AlF_6^{3-} is reduced at the cathode.
(B) Al is oxidized at the anode.
(C) Aluminum is converted from the -3 oxidation state to the 0 oxidation state.
(D) F^- acts as a reducing agent.
(E) F^- is reduced at the cathode.

35. A steady current of 10 amperes is passed through an aluminum-production cell for 15 minutes. Which of the following is the correct expression for calculating the number of grams of aluminum produced? (1 faraday = 96,500 coulombs)

(A) $\dfrac{(10)\,(15)\,(96{,}500)}{(27)\,(60)}$ g

(B) $\dfrac{(10)\,(15)\,(27)}{(60)\,(96{,}500)}$ g

(C) $\dfrac{(10)\,(15)\,(60)\,(27)}{(96{,}500)\,(3)}$ g

(D) $\dfrac{(96{,}500)\,(27)}{(10)\,(15)\,(60)\,(3)}$ g

(E) $\dfrac{(27)\,(3)}{(96{,}500)\,(10)\,(15)\,(60)}$ g

GO ON TO THE NEXT PAGE

Experiment	Initial [NO] (mol L^{-1})	Initial $[O_2]$ (mol L^{-1})	Initial Rate of Formation of NO_2 (mol $L^{-1}s^{-1}$)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

36. The initial-rate data in the table above were obtained for the reaction represented below. What is the experimental rate law for the reaction?

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

(A) Rate $= k[NO][O_2]$

(B) Rate $= k[NO][O_2]^2$

(C) Rate $= k[NO]^2[O_2]$

(D) Rate $= k[NO]^2[O_2]^2$

(E) Rate $= k\dfrac{[NO]}{[O_2]}$

Ionization Energies for element X (kJ mol^{-1})				
First	Second	Third	Fourth	Fifth
580	1,815	2,740	11,600	14,800

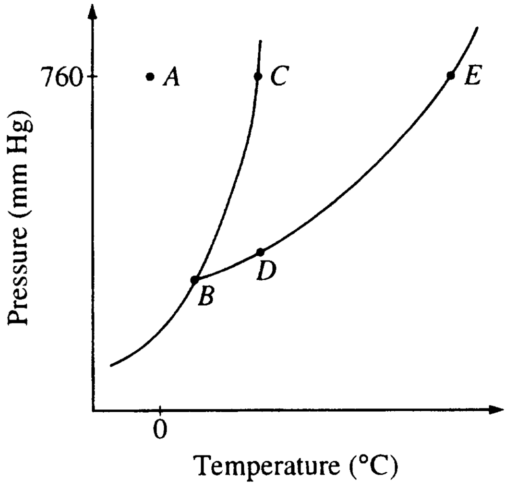
37. The ionization energies for element X are listed in the table above. On the basis of the data, element X is most likely to be

(A) Na
(B) Mg
(C) Al
(D) Si
(E) P

38. A molecule or an ion is classified as a Lewis acid if it

(A) accepts a proton from water
(B) accepts a pair of electrons to form a bond
(C) donates a pair of electrons to form a bond
(D) donates a proton to water
(E) has resonance Lewis electron-dot structures

GO ON TO THE NEXT PAGE



39. The phase diagram for a pure substance is shown above. Which point on the diagram corresponds to the equilibrium between the solid and liquid phases at the normal melting point?

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

40. Of the following molecules, which has the largest dipole moment?

(A) CO

(B) CO_2

(C) O_2

(D) HF

(E) F_2

$$2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g)$$

41. After the equilibrium represented above is established, some pure $O_2(g)$ is injected into the reaction vessel at constant temperature. After equilibrium is reestablished, which of the following has a lower value compared to its value at the original equilibrium?

(A) K_{eq} for the reaction

(B) The total pressure in the reaction vessel

(C) The amount of $SO_3(g)$ in the reaction vessel

(D) The amount of $O_2(g)$ in the reaction vessel

(E) The amount of $SO_2(g)$ in the reaction vessel

GO ON TO THE NEXT PAGE

$$\ldots Li_3N(s) + \ldots H_2O(l) \rightarrow \ldots Li^{+}(aq) + \ldots OH^{-}(aq) + \ldots NH_3(g)$$

42. When the equation above is balanced and all coefficients reduced to lowest whole-number terms, the coefficient for $OH^{-}(aq)$ is

(A) 1
(B) 2
(C) 3
(D) 4
(E) 6

43. A sample of 61.8 g of H_3BO_3, a weak acid, is dissolved in 1,000 g of water to make a 1.0-molal solution. Which of the following would be the best procedure to determine the molarity of the solution? (Assume no additional information is available.)

(A) Titration of the solution with standard acid
(B) Measurement of the pH with a pH meter
(C) Determination of the boiling point of the solution
(D) Measurement of the total volume of the solution
(E) Measurement of the specific heat of the solution

44. A rigid metal tank contains oxygen gas. Which of the following applies to the gas in the tank when additional oxygen is added at constant temperature?

(A) The volume of the gas increases.
(B) The pressure of the gas decreases.
(C) The average speed of the gas molecules remains the same.
(D) The total number of gas molecules remains the same.
(E) The average distance between the gas molecules increases.

45. What is the $H^{+}(aq)$ concentration in 0.05 M $HCN(aq)$? (The K_a for HCN is 5.0×10^{-10}.)

(A) 2.5×10^{-11} M
(B) 2.5×10^{-10} M
(C) 5.0×10^{-10} M
(D) 5.0×10^{-6} M
(E) 5.0×10^{-4} M

46. Which of the following occurs when excess concentrated $NH_3(aq)$ is mixed thoroughly with 0.1 M $Cu(NO_3)_2(aq)$?

(A) A dark red precipitate forms and settles out.
(B) Separate layers of immiscible liquids form with a blue layer on top.
(C) The color of the solution turns from light blue to dark blue.
(D) Bubbles of ammonia gas form.
(E) The pH of the solution decreases.

GO ON TO THE NEXT PAGE

47. When hafnium metal is heated in an atmosphere of chlorine gas, the product of the reaction is found to contain 62.2 percent Hf by mass and 37.4 percent Cl by mass. What is the empirical formula for this compound?

(A) HfCl
(B) $HfCl_2$
(C) $HfCl_3$
(D) $HfCl_4$
(E) Hf_2Cl_3

48. If 87.5 percent of a sample of pure ^{131}I decays in 24 days, what is the half-life of ^{131}I ?

(A) 6 days
(B) 8 days
(C) 12 days
(D) 14 days
(E) 21 days

49. Which of the following techniques is most appropriate for the recovery of solid KNO_3 from an aqueous solution of KNO_3 ?

(A) Paper chromatography
(B) Filtration
(C) Titration
(D) Electrolysis
(E) Evaporation to dryness

50. In the periodic table, as the atomic number increases from 11 to 17, what happens to the atomic radius?

(A) It remains constant.
(B) It increases only.
(C) It increases, then decreases.
(D) It decreases only.
(E) It decreases, then increases.

51. Which of the following is a correct interpretation of the results of Rutherford's experiments in which gold atoms were bombarded with alpha particles?

(A) Atoms have equal numbers of positive and negative charges.
(B) Electrons in atoms are arranged in shells.
(C) Neutrons are at the center of an atom.
(D) Neutrons and protons in atoms have nearly equal mass.
(E) The positive charge of an atom is concentrated in a small region.

52. Under which of the following sets of conditions could the most $O_2(g)$ be dissolved in $H_2O(l)$?

	Pressure of $O_2(g)$ Above $H_2O(l)$ (atm)	Temperature of $H_2O(l)$ (°C)
(A)	5.0	80
(B)	5.0	20
(C)	1.0	80
(D)	1.0	20
(E)	0.5	20

$$W(g) + X(g) \rightarrow Y(g) + Z(g)$$

53. Gases W and X react in a closed, rigid vessel to form gases Y and Z according to the equation above. The initial pressure of $W(g)$ is 1.20 atm and that of $X(g)$ is 1.60 atm. No $Y(g)$ or $Z(g)$ is initially present. The experiment is carried out at constant temperature. What is the partial pressure of $Z(g)$ when the partial pressure of $W(g)$ has decreased to 1.0 atm?

(A) 0.20 atm
(B) 0.40 atm
(C) 1.0 atm
(D) 1.2 atm
(E) 1.4 atm

GO ON TO THE NEXT PAGE

$$2\ NO(g) + O_2(g) \rightleftarrows 2\ NO_2(g) \qquad \Delta H < 0$$

54. Which of the following changes alone would cause a decrease in the value of K_{eq} for the reaction represented above?

(A) Decreasing the temperature
(B) Increasing the temperature
(C) Decreasing the volume of the reaction vessel
(D) Increasing the volume of the reaction vessel
(E) Adding a catalyst

$$10\ HI + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 5\ I_2 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O$$

55. According to the balanced equation above, how many moles of HI would be necessary to produce 2.5 mol of I_2, starting with 4.0 mol of $KMnO_4$ and 3.0 mol of H_2SO_4 ?

(A) 20.
(B) 10.
(C) 8.0
(D) 5.0
(E) 2.5

56. A yellow precipitate forms when 0.5 *M* NaI(*aq*) is added to a 0.5 *M* solution of which of the following ions?

(A) $Pb^{2+}(aq)$
(B) $Zn^{2+}(aq)$
(C) $CrO_4^{2-}(aq)$
(D) $SO_4^{2-}(aq)$
(E) $OH^{-}(aq)$

$$M(s) + 3\ Ag^+(aq) \rightarrow 3\ Ag(s) + M^{3+}(aq) \qquad E° = +\ 2.46\ V$$
$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E° = +\ 0.80\ V$$

57. According to the information above, what is the standard reduction potential for the half-reaction $M^{3+}(aq) + 3\ e^- \rightarrow M(s)$?

(A) −1.66 V
(B) −0.06 V
(C) 0.06 V
(D) 1.66 V
(E) 3.26 V

GO ON TO THE NEXT PAGE

58. On a mountaintop, it is observed that water boils at 90°C, not at 100°C as at sea level. This phenomenon occurs because on the mountaintop the

(A) equilibrium water vapor pressure is higher due to the higher atmospheric pressure
(B) equilibrium water vapor pressure is lower due to the higher atmospheric pressure
(C) equilibrium water vapor pressure equals the atmospheric pressure at a lower temperature
(D) water molecules have a higher average kinetic energy due to the lower atmospheric pressure
(E) water contains a greater concentration of dissolved gases

59. A 40.0 mL sample of 0.25 *M* KOH is added to 60.0 mL of 0.15 *M* $Ba(OH)_2$. What is the molar concentration of $OH^-(aq)$ in the resulting solution? (Assume that the volumes are additive.)

(A) 0.10 *M*
(B) 0.19 *M*
(C) 0.28 *M*
(D) 0.40 *M*
(E) 0.55 *M*

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(g)$$

60. A 0.03 mol sample of $NH_4NO_3(s)$ is placed in a 1 L evacuated flask, which is then sealed and heated. The $NH_4NO_3(s)$ decomposes completely according to the balanced equation above. The total pressure in the flask measured at 400 K is closest to which of the following? (The value of the gas constant, R, is 0.082 L atm mol^{-1} K^{-1}.)

(A) 3 atm
(B) 1 atm
(C) 0.5 atm
(D) 0.1 atm
(E) 0.03 atm

$$C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(g)$$

61. For the reaction of ethylene represented above, ΔH is −1,323 kJ. What is the value of ΔH if the combustion produced liquid water $H_2O(l)$, rather than water vapor $H_2O(g)$? (ΔH for the phase change $H_2O(g) \rightarrow H_2O(l)$ is −44 kJ mol^{-1}.)

(A) −1,235 kJ
(B) −1,279 kJ
(C) −1,323 kJ
(D) −1,367 kJ
(E) −1,411 kJ

GO ON TO THE NEXT PAGE

$$HC_2H_3O_2(aq) + CN^-(aq) \rightleftarrows HCN(aq) + C_2H_3O_2^-(aq)$$

62. The reaction represented above has an equilibrium constant equal to 3.7×10^4. Which of the following can be concluded from this information?

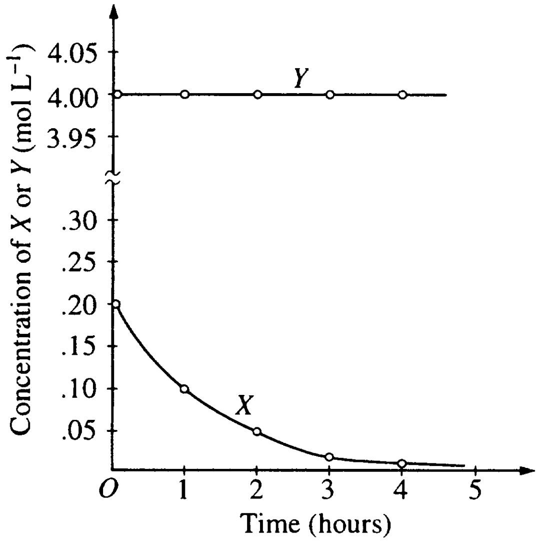
(A) $CN^-(aq)$ is a stronger base than $C_2H_3O_2^-(aq)$.

(B) $HCN(aq)$ is a stronger acid than $HC_2H_3O_2(aq)$.

(C) The conjugate base of $CN^-(aq)$ is $C_2H_3O_2^-(aq)$.

(D) The equilibrium constant will increase with an increase in temperature.

(E) The pH of a solution containing equimolar amounts of $CN^-(aq)$ and $HC_2H_3O_2(aq)$ is 7.0.



63. The graph above shows the results of a study of the reaction of X with a large excess of Y to yield Z. The concentrations of X and Y were measured over a period of time. According to the results, which of the following can be concluded about the rate law for the reaction under the conditions studied?

(A) It is zero order in $[X]$.
(B) It is first order in $[X]$.
(C) It is second order in $[X]$.
(D) It is first order in $[Y]$.
(E) The overall order of the reaction is 2.

GO ON TO THE NEXT PAGE

64. Equal numbers of moles of He(g), Ar(g), and Ne(g) are placed in a glass vessel at room temperature. If the vessel has a pinhole-sized leak, which of the following will be true regarding the relative values of the partial pressures of the gases remaining in the vessel after some of the gas mixture has effused?

(A) $P_{He} < P_{Ne} < P_{Ar}$
(B) $P_{He} < P_{Ar} < P_{Ne}$
(C) $P_{Ne} < P_{Ar} < P_{He}$
(D) $P_{Ar} < P_{He} < P_{Ne}$
(E) $P_{He} = P_{Ar} = P_{Ne}$

65. Which of the following compounds is NOT appreciably soluble in water but is soluble in dilute hydrochloric acid?

(A) $Mg(OH)_2(s)$
(B) $(NH_4)_2CO_3(s)$
(C) $CuSO_4(s)$
(D) $(NH_4)_2SO_4(s)$
(E) $Sr(NO_3)_2(s)$

66. When solid ammonium chloride, $NH_4Cl(s)$, is added to water at 25°C, it dissolves and the temperature of the solution decreases. Which of the following is true for the values of ΔH and ΔS for the dissolving process?

	ΔH	ΔS
(A)	Positive	Positive
(B)	Positive	Negative
(C)	Positive	Equal to zero
(D)	Negative	Positive
(E)	Negative	Negative

67. What is the molar solubility in water of Ag_2CrO_4 ? (The K_{sp} for Ag_2CrO_4 is 8×10^{-12}.)

(A) $8 \times 10^{-12}\ M$
(B) $2 \times 10^{-12}\ M$
(C) $\sqrt{4 \times 10^{-12}}\ M$
(D) $\sqrt[3]{4 \times 10^{-12}}\ M$
(E) $\sqrt[3]{2 \times 10^{-12}}\ M$

GO ON TO THE NEXT PAGE

68. In which of the following processes are covalent bonds broken?

(A) $I_2(s) \rightarrow I_2(g)$
(B) $CO_2(s) \rightarrow CO_2(g)$
(C) $NaCl(s) \rightarrow NaCl(l)$
(D) $C(\text{diamond}) \rightarrow C(g)$
(E) $Fe(s) \rightarrow Fe(l)$

69. What is the final concentration of barium ions, $[Ba^{2+}]$, in solution when 100. mL of 0.10 M $BaCl_2(aq)$ is mixed with 100. mL of 0.050 M $H_2SO_4(aq)$?

(A) 0.00 M
(B) 0.012 M
(C) 0.025 M
(D) 0.075 M
(E) 0.10 M

70. When 100 mL of 1.0 M Na_3PO_4 is mixed with 100 mL of 1.0 M $AgNO_3$, a yellow precipitate forms and $[Ag^+]$ becomes negligibly small. Which of the following is a correct listing of the ions remaining in solution in order of <u>increasing</u> concentration?

(A) $[PO_4^{3-}] < [NO_3^-] < [Na^+]$
(B) $[PO_4^{3-}] < [Na^+] < [NO_3^-]$
(C) $[NO_3^-] < [PO_4^{3-}] < [Na^+]$
(D) $[Na^+] < [NO_3^-] < [PO_4^{3-}]$
(E) $[Na^+] < [PO_4^{3-}] < [NO_3^-]$

71. In a qualitative analysis for the presence of Pb^{2+}, Fe^{2+}, and Cu^{2+} ions in aqueous solution, which of the following will allow the separation of Pb^{2+} from the other ions at room temperature?

(A) Adding dilute $Na_2S(aq)$ solution
(B) Adding dilute $HCl(aq)$ solution
(C) Adding dilute $NaOH(aq)$ solution
(D) Adding dilute $NH_3(aq)$ solution
(E) Adding dilute $HNO_3(aq)$ solution

72. After completing an experiment to determine gravimetrically the percentage of water in a hydrate, a student reported a value of 38 percent. The correct value for the percentage of water in the hydrate is 51 percent. Which of the following is the most likely explanation for this difference?

(A) Strong initial heating caused some of the hydrate sample to spatter out of the crucible.
(B) The dehydrated sample absorbed moisture after heating.
(C) The amount of the hydrate sample used was too small.
(D) The crucible was not heated to constant mass before use.
(E) Excess heating caused the dehydrated sample to decompose.

GO ON TO THE NEXT PAGE

73. The volume of distilled water that should be added to 10.0 mL of 6.00 *M* HCl(*aq*) in order to prepare a 0.500 *M* HCl(*aq*) solution is approximately

(A) 50.0 mL
(B) 60.0 mL
(C) 100. mL
(D) 110. mL
(E) 120. mL

74. Which of the following gases deviates most from ideal behavior?

(A) SO_2

(B) Ne

(C) CH_4

(D) N_2

(E) H_2

75. Which of the following pairs of liquids forms the solution that is most ideal (most closely follows Raoult's law) ?

(A) $C_8H_{18}(l)$ and $H_2O(l)$

(B) $CH_3CH_2CH_2OH(l)$ and $H_2O(l)$

(C) $CH_3CH_2CH_2OH(l)$ and $C_8H_{18}(l)$

(D) $C_6H_{14}(l)$ and $C_8H_{18}(l)$

(E) $H_2SO_4(l)$ and $H_2O(l)$

END OF SECTION I

IF YOU FINISH BEFORE TIME IS CALLED, YOU MAY CHECK YOUR WORK ON THIS SECTION.
DO NOT GO ON TO SECTION II UNTIL YOU ARE TOLD TO DO SO.

AP Chemistry Survey Questions

Time - 2 minutes

Answer the following questions and fill in the corresponding oval on the answer sheet. These questions are for research purposes only and will NOT influence the scoring of your examination.

76. For how many years (including your current course) have you taken chemistry in grades 9-12 ?

(A) None
(B) One-half year (one semester)
(C) One year (two semesters)
(D) One-and-a-half years (three semesters)
(E) Two years or more (four semesters or more)

77. If you have taken an AP Chemistry course, which of the following best describes it? (If you have NOT taken an AP Chemistry course, please skip to question 80.)

(A) A course scheduled for the full 1998-1999 school year
(B) A course meeting during the fall 1998 semester **only**
(C) A course meeting during the 1999 spring semester **only**
(D) A course taken **prior** to the 1998-1999 school year

78. On the average, how much time per week is scheduled for your AP Chemistry class?

(A) Fewer than 200 minutes
(B) Between 200-250 minutes
(C) Between 251-300 minutes
(D) More than 300 minutes

79. On the average, how much time do you spend per week in the laboratory for your AP Chemistry course? (Include extra time before or after school or during lunch or free periods.)

(A) 30 minutes or less
(B) 31 to 45 minutes
(C) 46 to 60 minutes
(D) 61 to 90 minutes
(E) More than 90 minutes

80. Which of the following best describes the type of calculator you will be using for Section II, Part A of this examination?

(A) Simple four-function (+,−,×,÷)
(B) Scientific (four functions plus log and trig functions), nonprogrammable
(C) Scientific, programmable, no graphing capabilities
(D) Graphing calculator with no stored chemistry equations or information
(E) Graphing calculator with stored chemistry equations and/or information

CHEMISTRY

SECTION II

Time—1 hour and 30 minutes

Percent of total grade—55

Part A: Time—40 minutes CALCULATORS, EXCEPT THOSE WITH TYPEWRITER (QWERTY) KEYBOARDS ARE ALLOWED. Programmable and graphing calculators may be used. Calculator memories need not be cleared of programs and data.

Parts B: Time—50 minutes NO CALCULATORS ARE ALLOWED.

General Instructions

The times for Part A and Part B will be announced separately. You may proceed freely from one question to the next within each part. Do not spend too much time on any one question.

Pages containing a periodic table, reduction potentials, and lists containing equations and constants are printed in the green insert and in the pink essay booklet for your use.

You may write your answers with either a pen or a pencil. Be sure to write CLEARLY and LEGIBLY. If you make an error, you may save time by crossing it out rather than trying to erase it. Write all your answers in the space provided following each question.

When you are told to begin, open your booklet and start work on Part A. When time is called, you must stop work and put away your calculator as directed. DO NOT start work on Part B until you are told to begin. Then, open your booklet to Part B and carefully tear out the green insert.

In this section of the examination, there is some choice as to which questions to answer. After you have completed the examination, you MUST circle the numbers of the questions you have selected in the box below to ensure that your choices are the questions that will be graded.

Part A	Part B
(Circle one.) 2 3	(Circle one.) 7 8

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

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.179
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.938	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	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** 95.94	43 **Tc** (98)	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** 121.75	52 **Te** 127.60	53 **I** 126.91	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** 183.85	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** 226.02	89 **†Ac** 227.03	104 **Unq** (261)	105 **Unp** (262)	106 **Unh** (263)	107 **Uns** (262)	108 **Uno** (265)	109 **Une** (266)									

*Lanthanide 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** 173.04	71 **Lu** 174.97
†Actinide Series:	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	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** (260)

GO ON TO THE NEXT PAGE

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$Li^+ + e^-$	$\rightarrow$	$Li(s)$	−3.05
$Cs^+ + e^-$	$\rightarrow$	$Cs(s)$	−2.92
$K^+ + e^-$	$\rightarrow$	$K(s)$	−2.92
$Rb^+ + e^-$	$\rightarrow$	$Rb(s)$	−2.92
$Ba^{2+} + 2e^-$	$\rightarrow$	$Ba(s)$	−2.90
$Sr^{2+} + 2e^-$	$\rightarrow$	$Sr(s)$	−2.89
$Ca^{2+} + 2e^-$	$\rightarrow$	$Ca(s)$	−2.87
$Na^+ + e^-$	$\rightarrow$	$Na(s)$	−2.71
$Mg^{2+} + 2e^-$	$\rightarrow$	$Mg(s)$	−2.37
$Be^{2+} + 2e^-$	$\rightarrow$	$Be(s)$	−1.70
$Al^{3+} + 3e^-$	$\rightarrow$	$Al(s)$	−1.66
$Mn^{2+} + 2e^-$	$\rightarrow$	$Mn(s)$	−1.18
$Zn^{2+} + 2e^-$	$\rightarrow$	$Zn(s)$	−0.76
$Cr^{3+} + 3e^-$	$\rightarrow$	$Cr(s)$	−0.74
$Fe^{2+} + 2e^-$	$\rightarrow$	$Fe(s)$	−0.44
$Cr^{3+} + e^-$	$\rightarrow$	Cr^{2+}	−0.41
$Cd^{2+} + 2e^-$	$\rightarrow$	$Cd(s)$	−0.40
$Tl^+ + e^-$	$\rightarrow$	$Tl(s)$	−0.34
$Co^{2+} + 2e^-$	$\rightarrow$	$Co(s)$	−0.28
$Ni^{2+} + 2e^-$	$\rightarrow$	$Ni(s)$	−0.25
$Sn^{2+} + 2e^-$	$\rightarrow$	$Sn(s)$	−0.14
$Pb^{2+} + 2e^-$	$\rightarrow$	$Pb(s)$	−0.13
$2H^+ + 2e^-$	$\rightarrow$	$H_2(g)$	0.00
$S(s) + 2H^+ + 2e^-$	$\rightarrow$	$H_2S(g)$	0.14
$Sn^{4+} + 2e^-$	$\rightarrow$	Sn^{2+}	0.15
$Cu^{2+} + e^-$	$\rightarrow$	Cu^+	0.15
$Cu^{2+} + 2e^-$	$\rightarrow$	$Cu(s)$	0.34
$Cu^+ + e^-$	$\rightarrow$	$Cu(s)$	0.52
$I_2(s) + 2e^-$	$\rightarrow$	$2I^-$	0.53
$Fe^{3+} + e^-$	$\rightarrow$	Fe^{2+}	0.77
$Hg_2{}^{2+} + 2e^-$	$\rightarrow$	$2Hg(l)$	0.79
$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Hg^{2+} + 2e^-$	$\rightarrow$	$Hg(l)$	0.85
$2Hg^{2+} + 2e^-$	$\rightarrow$	$Hg_2{}^{2+}$	0.92
$Br_2(l) + 2e^-$	$\rightarrow$	$2Br^-$	1.07
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow$	$2H_2O(l)$	1.23
$Cl_2(g) + 2e^-$	$\rightarrow$	$2Cl^-$	1.36
$Au^{3+} + 3e^-$	$\rightarrow$	$Au(s)$	1.50
$Co^{3+} + e^-$	$\rightarrow$	Co^{2+}	1.82
$F_2(g) + 2e^-$	$\rightarrow$	$2F^-$	2.87

GO ON TO THE NEXT PAGE

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

ATOMIC STRUCTURE

$$\Delta E = h\nu$$

$$c = \lambda \nu$$

$$\lambda = \frac{h}{mv}$$

$$p = mv$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

E = energy

ν = frequency

λ = wavelength

p = momentum

v = velocity

n = principal quantum number

m = mass

Speed of light, $c = 3.0 \times 10^{8}$ m s^{-1}

Planck's constant, $h = 6.63 \times 10^{-34}$ J s

Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J K^{-1}

Avogadro's number $= 6.022 \times 10^{23}$ molecules mol^{-1}

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

1 electron volt per atom = 96.5 kJ mol^{-1}

EQUILIBRIUM

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

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

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

$$= K_a \times K_b$$

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

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

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

$$\mathrm{pOH} = \mathrm{p}K_b + \log\frac{[\mathrm{HB}^+]}{[\mathrm{B}]}$$

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

$$K_p = K_c(RT)^{\Delta n},$$

where Δn = moles product gas − moles reactant gas

Equilibrium Constants

K_a (weak acid)

K_b (weak base)

K_w (water)

K_p (gas pressure)

K_c (molar concentrations)

THERMOCHEMISTRY

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

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

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

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

$$= -RT \ln K = -2.303\, RT \log K$$

$$= -n\mathcal{F}E^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + 2.303\, RT \log Q$$

$$q = mc\Delta T$$

$$C_p = \frac{\Delta H}{\Delta T}$$

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

E° = standard reduction potential

T = temperature

n = moles

m = mass

q = heat

c = specific heat capacity

C_p = molar heat capacity at constant pressure

1 faraday $\mathcal{F}$ = 96,500 coulombs

GO ON TO THE NEXT PAGE

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

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

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

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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

$$u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

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

$$KE \text{ per mole} = \frac{3}{2}RTn$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

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

$$\text{molality} = \text{moles solute per kilogram solvent}$$

$$\Delta T_f = iK_f \times \text{molality}$$

$$\Delta T_b = iK_b \times \text{molality}$$

$$\pi = \frac{nRT}{V}i$$

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{n\mathcal{F}}\ln Q = E^{\circ}_{\text{cell}} - \frac{0.0592}{n}\log Q \text{ @ } 25^{\circ}C$$

$$\log K = \frac{nE^{\circ}}{0.0592}$$

P = pressure
V = volume
T = temperature
n = number of moles
D = density
m = mass
v = velocity

u_{rms} = root-mean-square speed
KE = kinetic energy
r = rate of effusion
M = molar mass
π = osmotic pressure
i = van't Hoff factor
K_f = molal freezing-point depression constant
K_b = molal boiling-point elevation constant
Q = reaction quotient
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
E° = standard reduction potential
K = equilibrium constant

Gas constant, R = 8.31 J mol^{-1} K^{-1}
= 0.0821 L atm mol^{-1} K^{-1}
= 8.31 volt coulomb mol^{-1} K^{-1}
Boltzmann's constant, k = 1.38×10^{-23} J K^{-1}
K_f for H_2O = 1.86 K kg mol^{-1}
K_b for H_2O = 0.512 K kg mol^{-1}
STP = 0.000°C and 1.000 atm
Faraday's constant, $\mathcal{F}$ = 96,500 coulombs per mole of electrons

GO ON TO THE NEXT PAGE

CHEMISTRY—SECTION II

(Total time—90 minutes)

Part A

Time—40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, because you may earn partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures. Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

1. In aqueous solution, ammonia reacts as represented above. In 0.0180 M $NH_3(aq)$ at 25°C, the hydroxide ion concentration, $[OH^-]$, is 5.60×10^{-4} M. In answering the following, assume that temperature is constant at 25°C and that volumes are additive.

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

(b) Determine the pH of 0.0180 M $NH_3(aq)$.

(c) Determine the value of the base ionization constant, K_b, for $NH_3(aq)$.

(d) Determine the percent ionization of NH_3 in 0.0180 M $NH_3(aq)$.

(e) In an experiment, a 20.0 mL sample of 0.0180 M $NH_3(aq)$ was placed in a flask and titrated to the equivalence point and beyond using 0.0120 M $HCl(aq)$.

(i) Determine the volume of 0.0120 M $HCl(aq)$ that was added to reach the equivalence point.

(ii) Determine the pH of the solution in the flask after a total of 15.0 mL of 0.0120 M $HCl(aq)$ was added.

(iii) Determine the pH of the solution in the flask after a total of 40.0 mL of 0.0120 M $HCl(aq)$ was added.

GO ON TO THE NEXT PAGE

Answer EITHER Question 2 below OR Question 3 on the next page. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 20 percent.

2. Answer the following questions regarding light and its interactions with molecules, atoms, and ions.

   (a) The longest wavelength of light with enough energy to break the Cl–Cl bond in $Cl_2(g)$ is 495 nm.

      (i) Calculate the frequency, in s^{-1}, of the light.

      (ii) Calculate the energy, in J, of a photon of the light.

      (iii) Calculate the minimum energy, in kJ mol^{-1}, of the Cl–Cl bond.

   (b) A certain line in the spectrum of atomic hydrogen is associated with the electronic transition in the H atom from the sixth energy level ($n = 6$) to the second energy level ($n = 2$).

      (i) Indicate whether the H atom emits energy or whether it absorbs energy during the transition. Justify your answer.

      (ii) Calculate the wavelength, in nm, of the radiation associated with the spectral line.

      (iii) Account for the observation that the amount of energy associated with the same electronic transition ($n = 6$ to $n = 2$) in the He^+ ion is greater than that associated with the corresponding transition in the H atom.

GO ON TO THE NEXT PAGE

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

3. A rate study of the reaction represented above was conducted at 25°C. The data that were obtained are shown in the table below.

Experiment	Initial [NO] (mol L^{-1})	Initial $[Br_2]$ (mol L^{-1})	Initial Rate of Appearance of NOBr (mol L^{-1} s^{-1})
1	0.0160	0.0120	3.24×10^{-4}
2	0.0160	0.0240	6.38×10^{-4}
3	0.0320	0.0060	6.42×10^{-4}

(a) Calculate the initial rate of disappearance of $Br_2(g)$ in experiment 1.

(b) Determine the order of the reaction with respect to each reactant, $Br_2(g)$ and $NO(g)$. In each case, explain your reasoning.

(c) For the reaction,

(i) write the rate law that is consistent with the data, and

(ii) calculate the value of the specific rate constant, k, and specify units.

(d) The following mechanism was proposed for the reaction:

$Br_2(g) + NO(g) \rightarrow NOBr_2(g)$ *slow*

$NOBr_2(g) + NO(g) \rightarrow 2\,NOBr(g)$ *fast*

Is this mechanism consistent with the given experimental observations? Justify your answer.

GO ON TO THE NEXT PAGE

CHEMISTRY

Part B
Time—50 minutes

NO CALCULATORS MAY BE USED WITH PART B.

Answer Question 4 below. The Section II score weighting for this question is 15 percent.

4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. In all cases a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

   Example: A strip of magnesium is added to a solution of silver nitrate.

Ex.	$Mg + Ag^+ \rightarrow Mg^{2+} + Ag$

(a) Calcium oxide powder is added to distilled water.

(b) Solid ammonium nitrate is heated to temperatures above 300°C.

(c) Liquid bromine is shaken with a 0.5 *M* sodium iodide solution.

(d) Solid lead(II) carbonate is added to a 0.5 *M* sulfuric acid solution.

(e) A mixture of powdered iron(III) oxide and powdered aluminum metal is heated strongly.

(f) Methylamine gas is bubbled into distilled water.

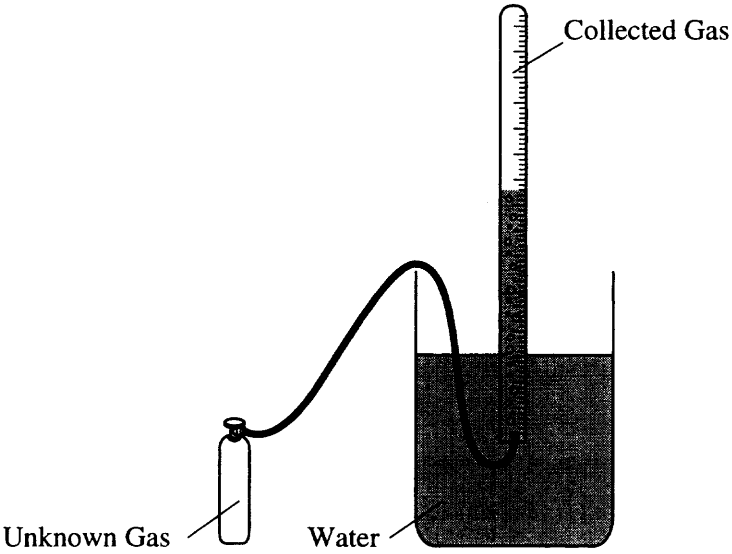
(g) Carbon dioxide gas is passed over hot, solid sodium oxide.

(h) A 0.2 *M* barium nitrate solution is added to an alkaline 0.2 *M* potassium chromate solution.

GO ON TO THE NEXT PAGE

Your responses to the rest of the questions in this part of the examination will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

Answer BOTH Question 5 below AND Question 6 on the next page. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).



5. A student performs an experiment to determine the molar mass of an unknown gas. A small amount of the pure gas is released from a pressurized container and collected in a graduated tube over water at room temperature, as shown in the diagram above. The collection tube containing the gas is allowed to stand for several minutes, and its depth is adjusted until the water levels inside and outside the tube are the same. Assume that:

    - the gas is not appreciably soluble in water
    - the gas collected in the graduated tube and the water are in thermal equilibrium
    - a barometer, a thermometer, an analytical balance, and a table of the equilibrium vapor pressure of water at various temperatures are also available.

    (a) Write the equation(s) needed to calculate the molar mass of the gas.

    (b) List the measurements that must be made in order to calculate the molar mass of the gas.

    (c) Explain the purpose of equalizing the water levels inside and outside the gas collection tube.

    (d) The student determines the molar mass of the gas to be 64 g mol^{-1}. Write the expression (set-up) for calculating the percent error in the experimental value, assuming that the unknown gas is butane (molar mass 58 g mol^{-1}). Calculations are not required.

    (e) If the student fails to use information from the table of the equilibrium vapor pressures of water in the calculation, the calculated value for the molar mass of the unknown gas will be smaller than the actual value. Explain.

GO ON TO THE NEXT PAGE

6. Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory.

(a) Consider the reaction represented below, which is spontaneous at 298 K.

$$CO_2(g) + 2\,NH_3(g) \rightarrow CO(NH_2)_2(s) + H_2O(l) \qquad \Delta H^\circ_{298} = -134 \text{ kJ}$$

(i) For the reaction, indicate whether the standard entropy change, ΔS°_{298}, is positive, or negative, or zero. Justify your answer.

(ii) Which factor, the change in enthalpy, ΔH°_{298}, or the change in entropy, ΔS°_{298}, provides the principal driving force for the reaction at 298 K? Explain.

(iii) For the reaction, how is the value of the standard free energy change, ΔG°, affected by an increase in temperature? Explain.

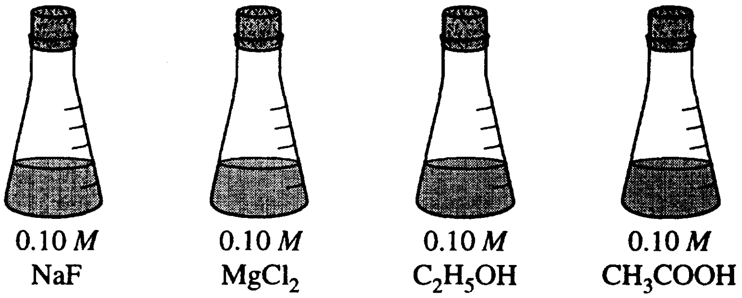
(b) Some reactions that are predicted by their sign of ΔG° to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.

(i) Account for this apparent contradiction.

(ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on ΔG° for the reaction? Explain.

GO ON TO THE NEXT PAGE

Answer EITHER Question 7 OR Question 8 below. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.



7. Answer the following questions, which refer to the 100 mL samples of aqueous solutions at 25°C in the stoppered flasks shown above.

   (a) Which solution has the lowest electrical conductivity? Explain.

   (b) Which solution has the lowest freezing point? Explain.

   (c) Above which solution is the pressure of water vapor greatest? Explain.

   (d) Which solution has the highest pH? Explain.

8. Answer the following questions using principles of chemical bonding and molecular structure.

   (a) Consider the carbon dioxide molecule, CO_2, and the carbonate ion, CO_3^{2-}.

      (i) Draw the complete Lewis electron-dot structure for each species.

      (ii) Account for the fact that the carbon-oxygen bond length in CO_3^{2-} is greater than the carbon-oxygen bond length in CO_2.

   (b) Consider the molecules CF_4 and SF_4.

      (i) Draw the complete Lewis electron-dot structure for each molecule.

      (ii) In terms of molecular geometry, account for the fact that the CF_4 molecule is nonpolar, whereas the SF_4 molecule is polar.

END OF EXAMINATION

Chapter III

Answers to the 1999 AP Chemistry Examination

- Examination Overview
- Section I: Multiple Choice
- Section II: Free Response
  - Student Preparation for the Exam
  - Free-Response Questions, Scoring Guidelines, and Sample Student Responses
  - Section II, Part A
  - Section II, Part B

Examination Overview

The 1999 AP Chemistry Examination consisted of two sections. Section I was made up of 75 multiple-choice questions worth 45 percent of the final exam grade; and Section II, worth 55 percent, contained eight free-response questions out of which students answered a total of six.

Section II was divided into two parts. In part A, which was 40 minutes long and for which students were allowed the use of a calculator, students worked on two quantitative problems (Question 1 and either Question 2 or Question 3). In Part B which was 50 minutes in length and for which no calculators were permitted, students answered Question 4 on predicting products of chemical reactions, Questions 5 and 6 (one laboratory-based plus one other, both required), and either Question 7 or Question 8.

Both the exam itself and student performance on the exam were rather typical in 1999. The percent of students earning an AP score of 3, 4, or 5 was also typical at about 65 percent. In general, the examination is relatively difficult for the population of examinees, which in part reflects the difficulty many college students encounter with this demanding subject.

More detailed information about the difficulty of the individual multiple-choice and free-response questions is provided in the following pages.

Section I: Multiple Choice

Listed below are the correct answers to the multiple-choice questions and the percentage of AP candidates who answered each question correctly.

Section I Answer Key and Percent Answering Correctly

Item No.	Correct Answer	Percent Correct by Grade					Total Percent Correct
		5	4	3	2	1	
1	C	96	90	79	65	45	74
2	E	82	66	48	34	19	48
3	B	66	54	42	33	24	42
4	A	93	85	76	63	48	71
5	D	94	90	82	69	40	75
6	A	98	94	86	73	42	78
7	C	83	70	58	45	22	55
8	E	99	96	91	81	55	83
9	C	82	67	56	42	26	52
10	E	76	56	42	26	12	41
11	A	70	46	28	15	11	33
12	B	69	47	33	22	14	35
13	A	94	81	63	45	27	60
14	B	94	84	69	52	33	64
15	D	94	86	72	52	29	65
16	C	92	82	67	49	23	61
17	E	87	82	75	67	49	70
18	A	87	81	75	61	35	67
19	C	85	77	73	68	62	73
20	B	87	77	61	39	23	55
21	B	46	36	31	26	21	33
22	E	94	89	77	62	30	68
23	E	80	73	69	63	55	67
24	D	39	24	18	13	10	20
25	C	81	69	59	48	35	57
26	C	83	78	77	73	61	74
27	A	31	19	15	11	6	16
28	B	74	66	56	45	33	53
29	E	45	32	26	19	13	26
30	D	93	88	83	72	43	75
31	C	38	26	19	14	11	21
32	D	73	54	37	23	15	38
33	C	93	78	58	36	19	54
34	A	73	54	44	29	16	42
35	C	80	63	43	29	17	43
36	B	90	75	58	34	15	52
37	C	65	49	34	20	13	35
38	B	68	48	39	25	20	38
39	C	95	89	80	64	34	71
40	D	86	71	57	39	26	54
41	E	92	85	75	55	28	65
42	C	85	77	74	67	56	71
43	D	80	72	63	55	39	60
44	C	86	73	60	41	22	54
45	D	79	58	41	21	12	40
46	C	37	24	20	15	16	22
47	C	80	66	52	36	20	50
48	B	74	58	43	29	18	42
49	E	78	63	55	45	32	53
50	D	80	73	68	57	36	62
51	E	86	76	64	51	29	59
52	B	58	42	31	20	14	31
53	A	80	61	46	32	20	46
54	B	66	47	35	22	15	35
55	D	93	82	74	63	46	69
56	A	60	43	29	21	14	32
57	A	72	56	46	35	21	44
58	C	75	55	38	23	14	39
59	C	59	41	25	13	15	28
60	A	53	26	13	11	11	22
61	E	62	43	31	19	9	31
62	A	74	45	25	12	10	31
63	B	64	46	32	21	17	34
64	A	87	80	68	57	40	65
65	A	59	41	32	26	20	35
66	A	68	44	29	13	9	31
67	E	65	38	18	9	6	25
68	D	81	65	52	40	34	54
69	C	62	35	24	19	21	31
70	A	73	48	27	16	12	34
71	B	63	40	28	18	18	32
72	B	45	27	21	18	18	25
73	D	58	43	30	23	18	33
74	A	85	66	50	31	16	48
75	D	57	37	26	20	20	33

Section II: Free Response

Student Preparation for the Exam

In this section of the examination, students answered a total of six free-response questions according to the format shown earlier on page 6. The table below shows the percentages of students choosing each question and the mean scores of the questions.

Student performance on the free-response questions this year was typical. The mean scores on the questions varied between 34 percent and 55 percent (with an average of 42 percent) of the maximum possible scores. More details of student performance are provided with the opening commentary for each individual question in the following section.

Free-Response Questions, Scoring Guidelines, and Sample Student Responses with Commentary

The answers presented here are actual student responses to the eight free-response questions on the 1999 AP Chemistry Examination. The students gave permission to have their work reproduced at the time they took the exam. These responses were read and scored by the leaders and faculty consultants assigned to each particular question and were used as sample responses for the training of faculty consultants during the AP Reading in June 1999. The actual scores that these students received, as well as a brief explanation of why, are indicated.

Commentary on Free-Response Question 1

This was a typical first-year college chemistry question dealing with ionic equilibria in aqueous solution. The first 5 points were quite fundamental, and are thoroughly covered in the first-year high school chemistry course. Despite this, the mean score was surprisingly low (3.43 out of 9), although about 2 percent of the students earned a perfect score on this question. Many students included water in their equilibrium expression in part (a). The majority of students calculated the correct pH in part (b) and about half found the correct value of K_b in part (c). Many others calculated the correct K value in part (a), but considered it to be K_a. They then used K_w to find K_b in part (c). A large number of students calculated the correct percent ionization, but many others found the percent of ammonia not ionized. Most students were able to calculate the correct volume of HCl needed to reach the equivalence point in part (e) i. Not many students recognized that in part (e) ii, the titration was halfway to the equivalence point. Some of those who did recognize this thought that this meant that the pH had to be 7 at the equivalence point. These students divided 7 by 2 to get the pH. Part (e) iii was answered more successfully by the students who attempted it. The most common mistake seen in the better responses was the failure to convert moles of H^+ to molarity of H^+ before finding the pH.

Percentages of Students Choosing Each Question and Mean Scores of Questions

Question Number	Question Type	Required/ Optional	Percent Choosing*	Mean Score (% of maximum)
1	Equilibrium Problem	Required	100	38
2	Quantitative Problem	Optional	26	37
3	Quantitative Problem	Optional	70	48
4	Reactions	Required	100	42
5	Laboratory Essay	Required	100	41
6	Other Essay	Required	100	40
7	Other Essay	Optional	14	34
8	Other Essay	Optional	83	55

*May not total 100 percent due to students omitting questions.

Scoring Guidelines for Free-Response Question 1

Question 1
(9 points)

(a) $K = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$ *1 pt*

(b) $[OH^-] = 5.60 \times 10^{-4} \Rightarrow \left\{ \begin{array}{c} pOH = 3.252 \\ \text{or} \\ [H^+] = 1.79 \times 10^{-11} \end{array} \right\} \Rightarrow pH = 10.748$ *1 pt*

(c) $K_b = \dfrac{(5.60 \times 10^{-4})^2}{0.0180 - 5.60 \times 10^{-4}} = 1.74 \times 10^{-5} \text{ (or } 1.80 \times 10^{-5}\text{)}$ *2 pts*

Note: 1st point for $[NH_4^+] = [OH^-] = 5.60 \times 10^{-4}$; 2nd point for correct answer

(d) $\%\text{ ionization} = \dfrac{5.60 \times 10^{-4}}{0.0180} \times 100\,\% = 3.11\% \text{ (or } 0.0311\text{)}$ *1 pt*

(e) $NH_3 + H^+ \rightarrow NH_4^+$

(i) mol $NH_3 = 0.0180\ M \times 0.0200\ L = 3.60 \times 10^{-4}$ mol = mol H^+ needed

vol HCl solution = $\dfrac{3.60 \times 10^{-4}\text{ mol}}{0.0120\ M} = 0.0300\ L = 30.0\ mL$ *1 pt*

(ii) mol H^+ added = mol $0.0120\ M \times 0.0150\ L = 1.80 \times 10^{-4}$ mol H^+ added
$= 1.80 \times 10^{-4}$ mol NH_4^+ produced

$[NH_4^+] = \dfrac{1.80 \times 10^{-4}\text{ mol}}{0.0350\ L} = 0.00514\ M = [NH_3]$ *1 pt*

Note: Point earned for 1.80×10^{-4} mol, or $0.00514\ M$ $[NH_3]$ or $[NH_4^+]$, or statement "halfway to equivalence point".

$K_b = 1.80 \times 10^{-5} = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = [OH^-] \Rightarrow pOH = 4.745 \Rightarrow pH = 9.255$ *1 pt*

$(= 1.74 \times 10^{-5})$ $(= 4.759)$ $(= 9.241)$

(iii) 10.0 mL past equivalence point

$0.0100\ L \times 0.0120\ M = 1.20 \times 10^{-4}$ mol H^+ in 60.0 mL

$[H^+] = \dfrac{0.000120\text{ mol}}{0.0600\ L} = 0.00200\ M$

$pH = -\log(2.00 \times 10^{-3}) = 2.700$ *1 pt*

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)

**number of significant figures must be correct within +/− <u>one</u> digit (except for pH: +/− <u>two</u> digits)*

Excellent Response (9 points)

(a) $\boxed{K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]}}$

(b) $[OH^-] = 5.60 \times 10^{-4}\ M$ $\qquad [H^+] = \frac{1 \times 10^{-14}}{5.60 \times 10^{-4}} = 1.8 \times 10^{-11}\ M$

$pH = -\log[H^+] = \boxed{10.7}$

(c) $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$ $\qquad NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$0.0180 M \quad — \quad 5.60 \times 10^{-4} \quad 5.60 \times 10^{-4} M$

$[NH_4^+] = [OH^-]$

$K_b = \frac{[5.60 \times 10^{-4}]^2}{[0.0180]} = \boxed{1.74 \times 10^{-5}}$

(d) % ionization $= \frac{[OH^-]}{[NH_3]} \times 100\%$

$= \frac{5.60 \times 10^{-4}}{0.0180} \times 100\% = \boxed{3.11\% \text{ ionized}}$

(e) (i) at equivalence point, (mol-acid) = (mol-base)

$\therefore$ $(20.0\ mL)(0.0180\ M\ NH_3) = V \cdot (0.0120\ M\ HCl)$

$V = \boxed{30.0\ mL}$

(ii) $H^+ + NH_3 \rightleftharpoons NH_4^+$ $\qquad$ stoichiometric shift

$(0.015 L)(0.0120 M) \quad (0.020 L)(0.0180 M) \quad 0$

$0.00018\ mol \quad 0.00036\ mol \quad 0$

$-0.00018\ mol \quad -0.00018\ mol \quad +0.00018\ mol$ $\qquad [NH_3] = [NH_4^+] = \frac{0.00018\ mol}{0.035 L}$

$0 \quad 0.00018\ mol \quad 0.00018\ mol$

$[NH_3]/[NH_4^+] = 1$ $\quad \therefore$ by Henderson-Hasselbach eqn, $pH = pK_a$

$K_a = 1 \times 10^{-14} \div K_b$ (from above) $= 5.7 \times 10^{-10}$

$pH = -\log K_a = \boxed{9.24}$

(iii) $H^+ + NH_3 \rightleftharpoons NH_4^+$

$0.00048\ mol \quad 0.00036\ mol \quad 0$ $\qquad$ There is $0.00012\ mol$ H^+ in excess

$[H^+] = \frac{0.00012\ mol}{0.040 L + 0.020 L} = 0.002 M$ $\qquad pH = -\log[H^+]$

$= \boxed{2.70}$

Commentary on Response

This response earned a score of 9. In part (c), no credit was lost for ignoring the negligible decrease in concentration of NH_3.

Good Response (7 points)

(a) $\boxed{K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]}}$

(b) $[OH^-] = 5.60 \times 10^{-4} M$

$[H^+] = \frac{1.00 \times 10^{-14}}{5.60 \times 10^{-4}} = 1.79 \times 10^{-11} M$

$pH = -\log(1.79 \times 10^{-11}) = \boxed{10.748}$

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

$K_b = \frac{(5.60 \times 10^{-4})^2}{(0.0180)} = 1.74 \times 10^{-5}$

$\boxed{K_b = 1.74 \times 10^{-5}}$

(d) $\% \text{ ionization} = \frac{[NH_4^+]}{[NH_3]} \times 100\%$

$= \frac{(5.60 \times 10^{-4})}{0.0180}$

$\boxed{= 3.11 \%}$

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

(e) (i) $n_{NH_3} = 0.02 L \times 0.0180 m = 3.6 \times 10^{-4} mol\ NH_3$

$\frac{3.6 \times 10^{-4} mol\ HCl}{0.0120 m} = 0.03 L$

$\boxed{30.0 mL\ HCl}$

(ii) $n_{HCl} = 0.015 L \times 0.0120 M = 1.8 \times 10^{-4} mol\ HCl$

$n_{NH_3} = (3.6 \times 10^{-4}) - (1.8 \times 10^{-4}) = \frac{1.8 \times 10^{-4} mol\ NH_3}{0.035 L} = 0.00514 m$

$1.74 \times 10^{-5} = \frac{[OH^-]^2}{0.00514}$

$[OH^-] = 3.00 \times 10^{-4}$

$\boxed{pH = 10.476}$

(iii) $n_{HCl} = 0.040 L \times 0.0120 m = 4.8 \times 10^{-4} mol$

$n_{HCl} = (4.8 \times 10^{-4}) - (3.6 \times 10^{-4}) = \frac{1.2 \times 10^{-4} mol}{0.06 L} = 0.00200 m\ HCl$

$5.75 \times 10^{-10} = \frac{[H^+]^2}{0.00200}$ $[H^+] = 1.07 \times 10^{-6}$

$\boxed{pH = 5.970}$

Commentary on Response

In part (e) ii, one point was earned for finding the correct $[NH_3]$ at equilibrium, but since the amount of NH_4^+ was not considered, the resulting pH is incorrect. In part (e) iii, the correct $[H^+]$ at equilibrium was found, but it was not used correctly to find the pH. The total score for this response was 7.

Fair Response (6 points)

a) $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

b) $pOH = -\log [OH^-]$

$pOH = -\log 5.60 \times 10^{-4}$

$pOH = 3.25$

$pH = 14.00 - 3.25$

$pH = 10.75$

c) $K_b = \frac{(5.60 \times 10^{-4})^2}{.0180}$

$K_b = 3.87 \times 10^{-6}$

d) $3.87 \times 10^{-6} = \frac{x^2}{.0180}$

$x = 2.64 \times 10^{-4}$

$\frac{2.64 \times 10^{-4}}{.0180} \times 100\% = \boxed{1.5\%}$

e) i) $pH = 9$

$9 = -\log [H^+]$

$1.0 \times 10^{-9} = [H^+]$

$.0180\ M \times \frac{\#\ moles}{.020}$

$moles = 3.6 \times 10^{-9}$ moles

equivalence pt = pH of 9.00

ii) $.0120(.015) = moles$

$\overline{.01} = 1.8 \times 10^{-4} = moles$

$NH_3 + H^+ \Rightarrow NH^+$

$3.6 \times 10^{-4} \quad \cancel{1.8 \times 10^{-4}}$

1.8×1

1.8×10^{-4}

$NH_3 \rightarrow N^{3-} + 3H^{+1}$

$1.8 \times 10^{-4} \quad 0 \quad 0$

$.035$

$3.87 \times 10^{-6} = \frac{x^2}{5.1 \times 10^{-3}}$

$x = 1.4 \times 10^{-4}$

$pH = -\log 1.4 \times 10^{-4}$

$pH = 3.85$

iii) $.0120(.040) = moles$

$4.8 \times 10^{-4} = moles$

$NH_3 + H^+ \rightarrow NH_4^+$

$\cancel{3.6 \times 10^{-4}} \quad 4.8 \times 10^{-4}$

$\underline{3.6 \times 10^{-4}}$

$\frac{1.2 \times 10^{-4}}{.060}$

$pH = -\log .002$

$pH = 2.70$

Commentary on Response

In this response, which earned a score of 6, one point was lost for a math error in part (c). No credit was lost in part (d) for using the incorrect value of K_b to find the percent ionization. In part (e) i the volume was not determined, and one point was earned in part (e) ii for finding the correct $[NH_3]$ at equilibrium.

Commentary on Free-Response Question 2

This, the less popular of the two optional problems, was chosen by a little more than one-fourth of the students. While the subject of this question (the wave nature of light, and the electronic structure of the H atom) is an important part of the AP Chemistry curriculum, it has not been the focus of an AP Chemistry free-response question in many years, so it may have come as a surprise to some students. The first 3 points were basic — involving a single concept and hinged on applications of appropriate formulas. The latter points were earned for showing understanding of more subtle concepts related to the Bohr atomic model. About 2 percent of the students choosing this question earned a perfect score on it. Surprisingly few students (perhaps less than 30 percent) were able to correctly convert wavelength to frequency in part (a) i, primarily because of being unfamiliar with the nanometers unit. However, most students were then able to determine the energy of 495 nm light in part (a) ii with the appropriate substitution of the answer from part (a) i. Only about 10 percent of the responses showed the ability to convert the energy/photon from part (a) ii into kJ/mol for part (a) iii. In part (b), students who understood the atomic structure of hydrogen performed commendably, though in part (b) i, a confusion between "absorbing" and "emitting" and their relationships to energy change was evident in many responses. Part (b) ii was approached from all angles. Occasionally the energy transition was calculated using eV as units, oftentimes only the energy of either $n = 2$ or $n = 6$ was used to subsequently calculate the wavelength, but most often the calculated energy difference was followed by some roundabout solution for determining the wavelength. The signs (positive vs. negative) of the energies and energy change for the transition were often confused. In general, the performance of students on this question underscores the need for teachers to to continually reinforce understanding and facility with units. Also, students need to be reminded that an equation by itself or a calculation without an interpretation does not *solely* support an argument or an explanation in their response.

Scoring Guidelines for Free-Response Question 2

Question 2
(9 points)

(a) (i) $\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{17}\ \text{nm/sec}}{495\ \text{nm}}$ (*or*, $= \frac{3.00 \times 10^{8}\ \text{m/sec}}{495 \times 10^{-9}\ \text{m}}$) $= 6.06 \times 10^{14}\ \text{sec}^{-1}$ ***1 pt***

(ii) $E = h\nu = (6.626 \times 10^{-34}\ \text{J sec})(6.06 \times 10^{14}\ \text{sec}^{-1}) = 4.02 \times 10^{-19}\ \text{J}$ ***1 pt***

(iii) $(4.02 \times 10^{-19}\ \text{J})(6.022 \times 10^{-23}\ \text{mol}^{-1})(0.00100\ \text{kJ/J}) = 242\ \text{kJ/mol}$ ***1 pt***

Note: No units required if answers are numerically same as above. No penalty if answers are correct with different units and units are explicitly indicated (*e.g.*, for part (ii), 4.02×10^{-22} kJ is acceptable)

(b) (i) Energy is emitted. ***1 pt***

The $n = 6$ state is at a higher energy than the $n = 2$ state. Going from a high energy state to a low energy state means that energy must be emitted. ***1 pt***

Note: The key idea is that the energy of the $n = 6$ state is higher (more excited) than the lower (less excited) $n = 2$ state. The argument that "e^- is farther away" at the $n = 6$ level is not accepted.

(ii) $E_2 = \frac{-2.178 \times 10^{-18}\ \text{J}}{2^2} = -5.45 \times 10^{-19}\ \text{J}$, $E_6 = \frac{-2.178 \times 10^{-18}\ \text{J}}{6^2} = -6.05 \times 10^{-20}\ \text{J}$

$\Delta E = E_6 - E_2 = -6.05 \times 10^{-20}\ \text{J} - (-5.45 \times 10^{-19}\ \text{J}) = 4.84 \times 10^{-19}\ \text{J}$

OR, ***1 pt***

$\Delta E = 2.178 \times 10^{-18}(\frac{1}{2^2} - \frac{1}{6^2})\ \text{J} = 2.178 \times 10^{-18}(0.2222)\ \text{J} = 4.84 \times 10^{-19}\ \text{J}$

Note: Point earned for determining the energy of transition.
Negative energies acceptable.

$E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$

OR, ***1 pt***

$\nu = \frac{E}{h} = \frac{4.84 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{J sec}} = 7.30 \times 10^{14}\ \text{sec}^{-1}$

Note: Point earned for writing or using $E = \frac{hc}{\lambda}$, or for calculating the frequency, ν

Scoring Guidelines for Free-Response Question 2 *(continued)*

(ii) *continued...*

$$\lambda = \frac{c}{\nu} = \frac{3.00\times10^{8}\ \text{m sec}^{-1}}{7.30\times10^{14}\ \text{sec}^{-1}} \times \frac{1\ \text{nm}}{10^{-9}\ \text{m}} = 411\,\text{nm}$$

OR, *1 pt*

$$\lambda = \frac{(6.626\times10^{-34}\ \text{J sec})(3.00\times10^{17}\ \text{nm sec}^{-1})}{4.84\times10^{-19}\ \text{J}} = 411\ \text{nm}$$

Note: Point earned for correct wavelength; $\lambda = 4.11 \times 10^{-7}$ m accepted.
Negative wavelength not accepted.

(iii) The positive charge holding the electron is greater for He^+, which has a 2+ nucleus, than for H with its 1+ nucleus. The stronger attraction means that it requires more energy for the electron to move to higher energy levels. Therefore, transitions from high energy states to lower states will be more energetic for He^+ than for H. *1 pt*

Note: Other arguments accepted, such as, "E is proportional to Z^2. Since $Z = 2$ for He^+ and $Z = 1$ for H, all energy levels in He^+ are raised (by a factor of 4)." Other accepted answers must refer to the increased charge on the He^+ nucleus, and NOT the mass.

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)

**number of significant figures must be correct within +/− one digit*

Excellent Response (9 points)

a i $\nu = c/\lambda$ $\quad \nu = \frac{3.00 \cdot 10^{8} \frac{m}{s}}{4.95 \cdot 10^{-7} m} = 6.06 \cdot 10^{14} s^{-1}$

ii $E = h\nu$ $\quad E = 6.63 \cdot 10^{-34} J \cdot s \cdot 6.06 \cdot 10^{14} s^{-1} = 4.02 \cdot 10^{-19} J$

iii $\frac{4.02 \cdot 10^{-19} J}{molecule} \times \frac{6.022 \cdot 10^{23} molecules}{mol} \times \frac{1 kJ}{1000 J} = 242 kJ/mol$

b. i. This is an energy emission. First, in order to produce a spectral line, the atom must emit energy in the form of light. Second, high energy levels have more potential energy than low energy levels. In order to satisfy the law of conservation of energy, when an electron goes down in energy levels, the lost potential energy must go somewhere. It is most probable that it is emitted as light.

ii $E = -2.178 \cdot 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) J$ $\quad$ n_1 is the initial energy level

$= -2.178 \cdot 10^{-18} \left(\frac{1}{6^2} - \frac{1}{2^2}\right) J$ $\quad$ n_2 is the final energy level

$= -2.178 \cdot 10^{-18} \left(\frac{1}{36} - \frac{1}{4}\right) J$ $\quad$ E is the energy of the emitted photon

$= -2.178 \cdot 10^{-18} \left(\frac{1}{36} - \frac{9}{36}\right) J$

$E = -2.178 \cdot 10^{-18} \left(\frac{-8}{36}\right) J = -2.178 \cdot 10^{-18} \left(\frac{-2}{9}\right) J = +4.84 \cdot 10^{-19} J$

$E = h\nu \quad \nu = \frac{E}{h} \quad \nu = \frac{+4.84 \cdot 10^{-19} J}{6.63 \cdot 10^{-34} Js} = 7.30 \cdot 10^{14} s^{-1}$

$\lambda = \frac{c}{\nu} = \frac{3.00 \cdot 10^{8} m/s}{7.30 \cdot 10^{14} s^{-1}} = 4.11 \cdot 10^{-7} m = 411 nm$

iii: The energy is greater because in order for the electron to go to a higher energy level it must escape the pull of the nucleus. The He^+ ion has an extra proton and a much higher attractive force. The potential energy at high energy levels is much greater in the He^+ ion than in the H atom

Commentary on Response

This response earned the full 9 points available for this question. In part (a), each equation and substitution was correct with the appropriate number of significant figures. In part (b) i, that the transition involved emission was stated immediately. For part (b) ii the student provided a clear analysis and carried out the substitutions and calculations correctly, arriving at the right answer. In part (b) iii, the student demonstrated a clear understanding of atomic structure and the reason for the increased energy associated with the transition in the He^+ ion.

Good Response (7 points)

(a.) (i) $c = \lambda \nu$ $\quad 495\ \text{nm} \times \frac{1 \times 10^{-9}\ \text{m}}{1\ \text{nm}} = 4.95 \times 10^{-7}\ \text{m}$

$3.0 \times 10^{8}\ \text{m/s} = (4.95 \times 10^{-7}\ \text{m})\,\nu$

$6.06 \times 10^{14}\ \text{s}^{-1} = \nu$

(ii) $E = h\nu$ OR $E = h\frac{c}{\lambda}$

$E = (6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(6.06 \times 10^{14}\ \text{s}^{-1})$

$E = 4.02 \times 10^{-19}\ \text{J}$

(iii) E/MOLE OF CT $= \frac{4.02 \times 10^{-19}\ \text{J}}{1\ \text{MOLE}} \times \frac{1\ \text{KJ}}{1000\ \text{J}} = 4.02 \times 10^{-22}\ \text{KJ/m}$

(b.) (i) IT EMITS ENERGY: BECAUSE THE ENERGY OF THE 10TH ENERGY LEVEL IS GREATER THAN ANY ENERGY LEVEL BELOW IT, THE MORE LOW THE LOWER ENERGY. SO IT MUST GIVE OF ENERGY, OR LIGHT, TO GO TO LOWER LEVELS.

(ii) ENERGY CHANGE $= E_{10} - E_{2}$

$\frac{-2.178 \times 10^{-18}}{36} - \frac{-2.178 \times 10^{-18}}{4} = 4.84 \times 10^{-19}\ \text{J}$

$E = h\nu$ OR $E = h\frac{c}{\lambda}$

$4.84 \times 10^{-19}\ \text{J} = (6.626 \times 10^{-34}\ \text{J}\cdot\text{s})\left(\frac{3 \times 10^{8}\ \text{m/s}}{\lambda}\right)$

$2.43 \times 10^{6}\ \text{m}^{-1} = \frac{1}{\lambda}$

$\lambda = 4.12 \times 10^{-7}\ \text{m}$

Commentary on Response

This response earned 2 of 3 points in part (a), which was missing the necessary use of Avogadro's number to convert kJ/photon to kJ/mol. Full number of points were earned for the first two parts of part (b), even though the final answer for (b) ii, which was appropriately labeled, was not given in nanometers as requested. Part (b) iii was not addressed in this response, which received a total score of 7 points.

Fair Response (5 points)

a i. $c = \lambda v$

$3.0 \times 10^{8} = 495 \times 10^{-9} \times v$

$v = 6.06 \times 10^{14}\ s^{-}$

ii $\Delta E = hv$

$= 6.63 \times 10^{-34} \times 6.06 \times 10^{14} = 4.02 \times 10^{-19}\ J$

iii 1 e⁻ volt/atom = 96.5 kJ/mol 2 atoms

$\frac{4.02 \times 10^{-19}}{1000} = x\ \frac{96.5\,kJ}{mol} = \frac{3.88\,kJ}{mol}$

b i. H atom emits energy - as an electron falls, energy is emitted. It is no longer in the excited state. A bright line appears on the spectrum due to emitted energy.

ii $E_n = \frac{-2.178 \times 10^{-18}\,J}{n^2} = \frac{-2.178 \times 10^{-18}}{4^2} = -1.36 \times 10^{-19}\ J$

iii The amount of energy is greater even though the same amount of electrons are present due to the fact that in the H atom, there is only one proton. In the He^+, there are two protons. With more protons, it emits more energy as the electron undergoes the electronic transition.

Commentary on Response

This response earned a total of 5 points. Part (a) iii was addressed incorrectly, and part (b) ii showed misunderstanding by the inappropriate use of the relevant equation. A point was earned in part (b) iii because the student indicated that the energy difference was due to additional proton in He^+.

Commentary on Free-Response Question 3

Almost three-quarters of the students chose this question, which was a traditional kinetics question in which data were provided on the rate of a specific chemical reaction under various conditions. Students then had to draw conclusions about the kinetics and the mechanism of the reaction. This question has the highest mean score of the three problems (Questions 1, 2, and 3). Apparently, many students were more familiar with certain standard kinetics problems and as a result scored better on parts (b) and (c) than on parts (a) and (d). Surprisingly few carried out the straightforward calculation in part (a). In part (b) most students readily found the order of $Br_2(g)$ by directly comparing experiments 1 and 2. However, many found it difficult to determine the order of $NO(g)$, either making computational errors or simply ignoring that $[Br_2]_{init}$ changed for each experiment. Students tried to hold $[Br_2]$ constant by doubling entire lines of data in the table to determine the rate order. In many instances, students already knew the rate law for this reaction, but made errors in trying to justify the order of [NO] as 2.

Provided that the rate law stated in part (c) was not inconsistent with earlier work, students were given full credit for calculation of units in part (c) and arguments in part (d) correctly based on the rate law they stated. In part (c) many students lost credit by incorrectly computing the units for the rate constant. A number of students wrote equilibrium constant expressions instead of rate laws. In part (d) students assumed that if the same chemicals (NO, Br_2) appeared in the reaction or rate law from part (c), consistency occurred. Many students did not present the rate law from the mechanism as an argument for inconsistency (*e.g.*, $[NO]^2$ in experimental data, but [NO] in slow step).

In general, many students had difficulty correctly relating stoichiometry to kinetics. As examples, many failed to recognize relationships of coefficients to comparative rates change of concentration of species, many treated the overall reaction as if it were a single step in the mechanism and assigned orders accordingly, and a significant number correctly added the reactions to determine that reactants in the overall equation were in the rate law, but failed to check the slow step for the correct order of each reactant.

Scoring Guidelines for Free-Response Question 3

Question 3
(9 points)

(a) Rate of $Br_2(g)$ loss occurs at ½ the rate of $NOBr(g)$ formation.

Rate of $Br_2(g)$ loss $= \dfrac{3.24\times10^{-4}\,M}{2\text{ sec}} = 1.62\times10^{-4}\,M\,\text{sec}^{-1}$ (or mol L^{-1} sec^{-1}) *1 pt*

<u>Note:</u> No penalty for missing units; ignore + or − signs

(b) Comparing experiments 1 and 2, [NO] remains constant, $[Br_2]$ doubles, and rate doubles; therefore, rate $\propto [Br_2]^1 \Rightarrow$ reaction is first-order with respect to $[Br_2]$. *1 pt*

$$\frac{6.38\times10^{-4}}{6.42\times10^{-4}} \cong 1 = \frac{k[\text{NO}]^x[\text{Br}_2]}{k[\text{NO}]^x[\text{Br}_2]} = \frac{k[0.0160]^x[0.0240]}{k[0.0320]^x[0.0060]} = \left(\frac{1}{2}\right)^x 4 = 1 \Rightarrow$$

$\frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow x = 2 \Rightarrow$ reaction is second-order with respect to [NO] *2 pts*

<u>Note:</u> One point earned for a proper set-up, comparing experiments 2 and 3 (as is shown here) or experiments 1 and 3. Second point earned for solving the ratios correctly and determining that the exponent = 2. Also, credit can be earned for a non-mathematical approach (*e.g.*, one point for describing the change in $[Br_2]$ and subsequent effect on rate, another point for describing the change in [NO] and subsequent effect on rate).

(c) (i) Rate $= k[\text{NO}]^2[\text{Br}_2]$ *1 pt*

Note: Point earned for an expression that is <u>not</u> <u>inconsistent</u> with the answer in part (b)

(ii) $k = \dfrac{\text{Rate}}{[\text{NO}]^2[\text{Br}_2]} = \dfrac{3.24\times10^{-4}\,M\,\text{sec}^{-1}}{(0.0160)^2(0.0120)\,M^3} = 105\,M^{-2}\,\text{sec}^{-1}$ (or 105 L^2 mol^{-2} sec^{-1}) *2 pts*

(Using rate of $Br_2(g)$ loss $= 1.62\times10^{-4}\,M\,\text{sec}^{-1} \Rightarrow k = 52.7\,M^{-2}\,\text{sec}^{-1}$ is also correct.)

<u>Note:</u> One point for solving for the value of the rate constant <u>consistent</u> with the rate-law expression found in part (b) or stated in part (c); one point for the correct units <u>consistent</u> with the rate-law expression found in part (b) or stated in part (c).

(d) No, it is not consistent with the given experimental observations. *1 pt*

This mechanism gives a reaction that is first-order in [NO], and first-order in $[Br_2]$, as those are the two reactants in the rate-determining step. Kinetic data show the reaction is second-order in [NO] (and first-order in $[Br_2]$), so this cannot be the mechanism. *1 pt*

<u>Note:</u> One point earned for "No" [or for "Yes" if rate $= k[\text{NO}][\text{Br}_2]$ in part (b)].
One point earned for justifying why this mechanism is inconsistent with the observed rate-law [or consistent with rate law stated earlier in response].

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)
**number of significant figures must be correct within +/−<u>one</u> digit*

Excellent Response (9 points)

a) $R_{disp}\,Br_2 = \frac{1}{2}(R_{app}\,NOBr) = \frac{1}{2}(3.24E{-4}\,\frac{mol}{L\,s}) = \underline{1.62E{-4}\ ^{mol}/_{L\cdot s}}$

b) $R = k[NO]^{I}[Br_2]^{II}$

Use experiment #1,2: $3.24E{-4} = k[\overset{.016}{\cancel{NO}}]^{I}[\overset{.012}{\cancel{Br_2}}]^{II}$ Doubling of rate when

$6.38E{-4} = k[.016]^{I}[.024]^{II}$ doubling of $[Br_2]_0$.

$\sim 2 = (.024/.012)^{II} = (2)^{II}$ $\underline{II = 1}$

Use experiment #1,3: $6.42E{-4} = k[.032]^{I}[.006]^{1}$ Doubling of rate when

$3.24E{-4} = k[.016]^{I}[.012]^{1}$ quadrupling of $[NO]_0$ and

$\sim 2 = (.032/.016)^{I}(1/2) = 2^{I}/2$ $\underline{I = 2}$ halving of $[Br_2]_0$.

$\underline{R = k[NO]^2[Br_2]}$

c) i) $R = k[NO]^2[Br_2]$

ii) Use experiment #1 and plug in numbers:

$3.24E{-4} = k(.016)^2(.012)$ $k = 105$

$^{mol}/_{L\cdot s} = x(^{mol}/_{L})^2(^{mol}/_{L})$ $x = {}^{\cancel{mol}}/_{\cancel{L}s} \cdot {}^{L^2}/_{mol^2} \cdot {}^{\cancel{L}}/_{\cancel{mol}} = {}^{L^2}/_{mol^2 s}$

$k = \underline{105\ ^{L^2}/_{mol^2\cdot s}}$

d) No. This mechanism is <u>not</u> consistent with data because $NO_{(g)}$ comes into play in Mechanism #1, the slow mechanism, as a <u>first order</u>. Since fast reactions do not contribute significantly to the overall rate law, and $NO_{(g)}$ is <u>shown</u> to be actually <u>second</u> order for overall, this contradicts the mechanism, which shows both $NO_{(g)}$ and $Br_{2(g)}$ as being first <u>order</u>.

Commentary on Response

This response earned a full score of 9 points. Part (c) demonstrates excellent work with units.

Good Response (7 points)

A. $\text{Rate} = \frac{2[Br_2]}{\Delta t}$

B. With respect to NO, the reaction order is 2 because the coefficient of NO will be the power to which it is raised. Therefore, the order of the reaction with respect to Br_2 will be 1 because its coefficient is 1.

C.

(I) $\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}[NO]^x[Br_2]^2}{\cancel{k}[NO]^x[Br_2]^2} \rightarrow \frac{6.38\times10^{-4}}{3.24\times10^{-4}} = \left(\frac{0.0160}{0.0160}\right)^x\left(\frac{0.0240}{0.0120}\right)^z$

$1.97 = 2^z \rightarrow z = \frac{\log 1.97}{\log 2} = 1$ $\boxed{z=1}$

$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[NO]^x[Br_2]^1}{\cancel{k}[NO]^x[Br_2]^1} \rightarrow \frac{6.42\times10^{-4}}{6.38\times10^{-4}} = \left(\frac{0.0320}{0.0160}\right)^x\left(\frac{0.0060}{0.0240}\right)^1$

$1.01 = 2^x \cdot 0.250$

$4.04 = 2^x. \rightarrow x = \frac{\log 4.04}{\log 2} = 2$ $\boxed{x=2}$

Therefore, $\boxed{\text{Rate} = k[NO]^2[Br_2]}$

(II) $\text{Rate} = k[NO]^2[Br_2]$

$3.24\times10^{-4}\ \frac{mol}{L\cdot s} = k\left(0.0160\ \frac{mol}{L}\right)^2\left(0.0120\ \frac{mol}{L}\right)$

$3.24\times10^{-4}\ \frac{mol}{L\cdot s} = k\left(0.000192\ \frac{mol^3}{L^3}\right)$

$k = 1.69\ \frac{L^2}{mol^2\cdot s}$ $\boxed{k = 1.69\ L^2\cdot mol^{-2}\cdot s}$

D. $Br_{2(g)} + NO_{(g)} \rightarrow \cancel{NOBr_{2(g)}}$

$\cancel{NOBr_{2(g)}} + NO_{(g)} \rightarrow 2NOBr_{(g)}$

$2NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$

Condition 1: All elementary steps must add to produce overall equation. Since this does, condition 1 is met.

slow: $Br_{2(g)} + NO_{(g)} \rightarrow NOBr_{2(g)}$

$\text{Rate} = k[Br_2][NO]$

Condition 2: Rate law for slow elementary step must equal rate law for total equation. Since these two don't equal, 2nd requirement is not met.

$\boxed{\text{This mechanism is not consistent.}}$

Commentary on Response

Part (a), though indicating an appropriate relationship to use, did not provide a complete calculation. Despite the incorrect reason initially cited in part (b), full credit was earned for this part because of the detailed account for the orders provided in part (c). A point is lost in part (c) for a math error (neglecting to square the [NO] value), and both points are earned for part (d). The total score earned was 7 points.

Fair Response (5 points)

a) rate of disappearance of $Br_2(g)$:

$$\frac{3.24 \times 10^{-4}}{2} = \boxed{1.62 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}}$$

b) NO $\frac{0.0320}{0.0160} = 2$ $\frac{6.42 \times 10^{-4}}{6.38 \times 10^{-4}} = 1.01$

The order of the reaction for NO(g) is 0 because the rate doubles while the rate of appearance of NOBr remains approximately the same.

Br_2 $\frac{0.0240}{0.0120} = 2$ $\frac{6.38 \times 10^{-4}}{3.24 \times 10^{-4}} = 1.96 \approx 2$ $2^x = 2$

$x = 1$

The order of the reaction for Br_2 is 1 because as the concentration of Br_2 doubles, the rate of appearance of NOBr also doubles. Therefore, the equation $2^x = 2$ shows the order to be 1.

c) (i) $r = k[NO]^0[Br_2]^1$ or $r = k[Br_2]^1$

(ii) $r = k[Br_2]^1$

$3.24 \times 10^{-4} = k[0.0120]$

$k = 0.027$ seconds

d) Yes, this mechanism is consistent with the given experimental observations. The mechanism shows the overall equation to be:

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

Balancing the equation gives the following equation:

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

This equation is the same as the equation in the experimental observations.

Commentary on Response

In part (b) of this response, the student neglected to account for the change in initial $[Br_2]$ when comparing experiments 2 and 3. However, the student then correctly concluded that the order with respect to NO must be zero, and so one point out of the two possible was earned. The answer arrived at in part (c) was consistent with the student's derived rate law, but one point was lost for incorrect units. No credit was earned in part (d) because the proposed mechanism is inconsistent with the student's rate law derived in part (c).

Commentary on Free-Response Question 4

This was the traditional "reactions" question. In this question, students are given a description of a chemical situation (e.g. "sodium oxide is added to water" or "ethene gas is burned in air") and required to give the chemical formula(s) for the reactant(s) and to predict, and give the chemical formula(s), for the product(s). They are required to answer 5 of the 8 choices.
As in previous years, this question revealed how difficult equation-writing is for many students.
The mean score was 6.36 out of a possible 15 points. Many students wasted time by balancing the equations and by including the phase symbols. Common errors resulted from students' incomplete knowledge of monatomic and polyatomic ions and their charges. Some students failed to distinguish between reactions that occurred in aqueous solutions and those that did not, resulting in the prediction of ions in solution where no solution existed.

It is important for AP Chemistry students to learn the skills of writing chemical formulas (given the names of substances) and predicting the chemistry that occurs when the substances react. These skills can be mastered by frequent practice in writing net-ionic equations for reactions. Also important is experience in the laboratory, where students can observe and understand the descriptive chemistry needed to predict the products of reactions. Teachers can help students prepare for this question by reminding them about common patterns in the types of chemical reactions (such as acid-base, precipitation, oxidation-reduction, etc.). Also, a mastery of solubility characteristics is essential, as is a knowledge of the formulas and charges of common polyatomic ions. Students should also be aware that they have access to both a periodic table and a table of standard reduction potentials as they answer this question.

Scoring Guidelines for Free-Response Question 4

Question 4
(15 points)

Students choose five of the eight reactions. Only the answers in the boxes are graded (unless clearly marked otherwise). Each correct answer earns 3 points, 1 point for reactants and 2 points for products. All products must be correct to earn both product points. Equations do not need to be balanced and phases need not be indicated. Any spectator ions on the reactant side nullify the 1 possible reactant point, but if they appear again on the product side, there is no product-point penalty. A fully molecular equation (when it should be ionic) earns a maximum of one point. Ion charges must be correct.

(a) $CaO + H_2O \rightarrow Ca(OH)_2$

- *No penalty for the set of products { Ca^{2+}, OH^-, and $Ca(OH)_2$ }*

(b) $NH_4NO_3 \rightarrow N_2 + O_2 + H_2O$

OR

$NH_4NO_3 \rightarrow N_2O + H_2O$

- *Two points earned for $NH_4NO_2 \rightarrow N_2 + H_2O$*
- *No penalty for other oxides of nitrogen (e.g., NO, NO_2, N_2O_3, N_2O_4 – but not N_2O_5)*

(c) $Br_2 + I^- \rightarrow Br^- + I_2$

(d) $PbCO_3 + H^+ + HSO_4^-$ (or SO_4^{2-}) $\rightarrow PbSO_4 + CO_2 + H_2O$ (or HCO_3^-)

- *No reactant point earned for H_2SO_4*
- *No product point earned for H_2CO_3*

(e) $Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$

- *No penalty for the set of products { FeO, Fe, and Al_2O_3 }*

(f) $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$

- *Two points earned for $MeNH_2 + H_2O \rightarrow MeNH_3^+ + OH^-$*

(g) $CO_2 + Na_2O \rightarrow Na_2CO_3$

(h) $Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4$

Excellent Response (15 points)

a	$CaO + H_2O \rightarrow Ca(OH)_2$
b	$NH_4NO_3 \rightarrow NO_2 + H_2O$
d	$PbCO_3 + H^+ + HSO_4^- \rightarrow PbSO_4 + CO_2 + H_2O$
e	$Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$
h	$Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4$

Commentary on Response

This response was beautifully done and earned all 15 points available for this question.

Good Response (12 points)

a $CaO + H_2O \longrightarrow Ca(OH)_2$

$NH_4NO_3 \longrightarrow NH_3 + H^+ + NO_3^-$

b $NH_4NO_3 \longrightarrow NH_3 + H^+ + NO_3^-$

$Br_2 + Na^+ + I^-$

c $Br_2 + I^- \longrightarrow Br^- + I_2$

$PbCO_3 + H^+ + HSO_4^- \longrightarrow PbSO_4 + H_2CO_3$

d $PbCO_3 + H^+ + HSO_4^- \longrightarrow PbSO_4 + H_2CO_3$

$Fe_2O_3 + Al \longrightarrow Fe + Al_2O_3$

e $Fe_2O_3 + Al \longrightarrow Fe + Al_2O_3$

Commentary on Response

Full credit (3 points) was earned for each of the equations in (a), (c), and (d). In (b), the student appeared to confuse thermal decomposition with dissociation of salts in solution, and no product points were earned. In (d), one product point was lost for including the unstable species H_2CO_3 as a product. The total score earned by this response was 12 points.

Fair Response (7 points)

a	$CaO + H_2O \rightarrow H_2CaO_2$

c	$Br + NaI \rightarrow NaB + I_2$

g	$CO_2 + NaO \rightarrow NaCO_3$

e	$Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$

b	$NH_4NO_3 \rightarrow NH_3 + HNO_3$

Commentary on Response

This response earned a total of 7 points. Only the reactant point was earned in (a) and in (b). Full credit was earned for the equation in (e), and one of the two possible reactant points were earned in each of (c) and (g).

Commentary on Free-Response Question 5

This was the first year that AP students and teachers knew that one of the mandatory essays would be a laboratory-based question. The goal of the laboratory-based question is to determine whether students understand how an experiment works, as well as the chemistry behind it. The mean score on this question was 3.33. The most difficult point to earn was the point for the mass of the gas in part (b) — many students mentioned "mass of the gas" but did not include which measurements were needed to obtain it. Frequently, when indicating how to determine the mass of the gas, many students considered the collection apparatus rather than the pressurized container. The second most difficult point to earn occurred in part (c). Many students had difficulty in recognizing that the water levels were equalized inside and outside the collection tube so that the *pressure* in the tube was equal to atmospheric pressure. Some examples of phrases that were not accepted in part (c) were "constant," "stable," "equilibrium," or "correct" pressure. In part (e), many students had difficulty in handling the explanation of why the calculated molar mass would be too low. Incorrect explanations varied, revealing no single most common misconception.

Overall, the performance of students on this question was good. Based on the responses to part (e), it is advisable for teachers to emphasize the importance of error analysis associated with laboratory. In discussions of error analysis it would be valuable to include how different errors in measurements affect the final results, the difference between percent error and percent yield, and the distinction between measured and calculated quantities.

Scoring Guidelines for Free-Response Question 5

Question 5
(8 points)

(a) $PV = nRT$ *AND* $n = \frac{m}{M}$, *OR* *molar mass* = $\frac{mRT}{PV}$, *OR* $M = \frac{DRT}{P}$ — *1 pt*

(b) temperature, atmospheric pressure, volume of the gas, and mass of gas (mass of pressurized container before and after releasing the gas) — *3 pts*

<u>Note:</u> 1 point earned for any <u>two</u> of the above, 2 points earned for any <u>three</u> of them. "The mass of the gas" is acceptable as a "measurement" for the 1st or 2nd point. Extraneous measurements (*e.g.*, density, volume of liquid, etc.) are ignored. To earn 3rd point, "mass of pressurized container before and after releasing the gas", or "change in mass of container" must be indicated.

(c) to equalize internal pressure with room pressure (atmospheric pressure), or the pressure(s) will be the same. — *1 pt*

(d) % error = $\frac{(64 - 58)\,g}{58\,g} \times 100\,\%$ (or $\frac{6}{58} \times 100\%$, or $\frac{6}{58}$) — *1 pt*

<u>Note:</u> No points earned for generic response (*e.g.*, $\frac{|(\text{expt.} - \text{theor.})|}{\text{theor.}} \times 100$),

or for $\frac{6}{64} \times 100\,\%$. No penalty if "× 100%" is absent or if value (10%) is not calculated.

(e) Pressure will be larger, therefore number of moles will be larger — *1 pt*

molar mass = $\frac{\text{mass}}{\text{moles}}$, therefore calculated molar mass will be smaller — *1 pt*

OR, $M = \frac{mRT}{PV}$ (or $M = \frac{DRT}{P}$), and the denominator, *PV*, will be too large. — *2 pts*

Therefore, the value of the molar mass (= $\frac{mRT}{PV}$ or $\frac{DRT}{P}$) will be too small.

OR, The pressure is larger, or the number of moles is larger, or since $P_{total} = (P_{unknown} - P_{water})$ we know that $P_{total} > P_{unknown}$. — *1 pt only*

<u>Note:</u> If $n = \frac{m}{M}$ is missing in part (a) but present in part (e), 1 point is earned for part (a).

Excellent Response (8 points)

a) $PV = nRT$

$n = \frac{\text{grams of gas used}}{MM}$

↗ rearrange this equation to calculate the molar mass (MM)

b) Measurements needed

1. Atmospheric pressure (barometer)
2. Vapor Pressure (tables)
3. Temperature in Kelvin (thermometer)
4. Volume of gas collected (graduated tube)
5. Mass of pressurized container before and after the experiment—the difference is the grams used (analytic balance)

c) Equalizing the pressure is the only way you can measure the pressure of inside the tube, because then you know the pressure inside the tube equals the atmospheric pressure.

d) $\text{percent error} = \frac{|\text{actual value} - \text{experimental value}|}{\text{actual value}} \times 100\%$

in this case

$\text{percent error} = \frac{|58g - 68g|}{58g} \times 100$

e) If the student fails to subtract the vapor pressure from the atmospheric pressure, the pressure he uses in his calculations would be higher than the actual pressure, so using the ideal Gas law

$PV = nRT \Rightarrow \frac{PV}{RT} = n$ he will get a higher value for n, so when he divides the grams of gas by n, the molar mass will be lower.

Commentary on Response

This response exemplifies a complete answer to the question and earned the full score of 8 points.

Good Response (6 points)

(a) $PV = nRT$

$PV = \frac{m}{M}RT$

$M = \frac{m\,RT}{V \cdot P} = D\frac{RT}{P}$

(b) density of gas collected , volume of gas.
pressure
temperature

(c) By equalizing the water levels inside & outside the gas collection tube. the pressure difference would not have to account for the difference in volume.

(d) $\frac{|64\text{g/mol} - 58\text{g/mol}|}{58\text{g/mol}} \times 100\%$

(e) Without using information from the table of the equilibrium vapor pressures of water, the pressure will be higher than expected, which will give a larger denominator to the equation $D\frac{RT}{P} = M$. The resulting molar mas will then be lower than expected.

Commentary on Response

This response earned all but 2 of the possible 8 points. In part (b), "density" did not earn the point — an explicit statement about mass was required. No credit was earned for part (c), which failed to describe an equalization of pressures.

Fair Response (4 points)

a) molar mass = $\frac{dRT}{P}$

b) in order to calculate the molar mass of the gas, measurements of the density, temperature, and pressure must be made

c) the purpose of equalizing water levels is to make sure the same amount of pressure is exerted on each

d) $\%\text{error} = \frac{(64\ \text{g mol}^{-1}) - (58\ \text{g mol}^{-1})}{58\ \text{g mol}^{-1}}$

e) the molar mass of the unknown gas will be smaller than the actual value because the measured value of vapor pressure are different

Commentary on Response

In part (b) only one point was earned since neither mass nor volume was explicitly mentioned. No credit was earned in part (e), since the response was essentially a restatement of the question and did not address the relationship between the measured pressure and the molar mass. The total score for this response was 4 points.

Commentary on Free-Response Question 6

This question dealt with the two fundamental topics that control chemical reactivity, thermodynamics and kinetics. While fundamental, these topics are often taught at different times of the year in the AP course, and many students seemed to have difficulty switching gears from one topic to the other. The mean score on this question was 3.2, and the most common (modal) score 2.

For part (a) i, a frequently seen error was students reversing "cause and effect" and reasoning that since the reaction was spontaneous, $\Delta S°$ must be positive. In part (a) ii, one point was earned for identifying $\Delta H°$ as the driving force, with a second point earned for a valid justification. Most responses that answered part (a) i correctly also earned at least one point here, but a frequent error was failure to phrase the justification in terms of the negative sign of $\Delta S°$ and claim that a negative $\Delta H°$ was sufficient to drive the reaction. In part (b) i, students were required to recognize the distinction between spontaneity and rate and to justify the fact that spontaneous reaction may occur quite slowly. Most papers effectively separated the concepts of spontaneity and rate; however, many papers did not present a sufficient justification. The phrase "thermodynamics does not imply kinetics," or "a spontaneous reaction may proceed quite slowly" was a common restatement of the question and did not earn the point here. In part (b) ii, due to the common confusion among the concepts of E_{act}, $\Delta H°$, and $\Delta G°$, many students made the erroneous claim that a more spontaneous reaction must have a more negative value of $\Delta G°$.

Scoring Guidelines for Free-Response Question 6

Question 6
(8 points)

(a) (i) $\Delta S°$ is negative (–) **OR** $\Delta S° < 0$ **OR** entropy is decreasing. ***1 pt***

3 moles of gaseous particles are converted to 2 moles of solid/liquid. ***1 pt***

- *One point earned for correct identification of (–) sign of* $\Delta S°$
- *One point earned for correct explanation (mention of phases is crucial for point)*
- *No point earned if incorrect* $\Delta S°$ *sign is obtained from the presumed value of* $\Delta G°$

(ii) $\Delta H°$ drives the reaction. ***1 pt***

The decrease in entropy ($\Delta S° < 0$) cannot drive the reaction, so the decrease in enthalpy ($\Delta H° < 0$) MUST drive the reaction.

OR ***1 pt***

$\Delta G° = \Delta H° - T\Delta S°$; for a spontaneous reaction $\Delta G° < 0$, and a negative value of $\Delta S°$ causes a positive $\Delta G°$.

- *One point earned for identifying* $\Delta H°$ *as the principal driving force for the reaction*
- *One point earned for correct justification*
- *Justification point earned by mentioning the effects of changes in entropy and enthalpy on the spontaneity of the reaction OR by a mathematical argument using the Gibbs-Helmholtz equation and some implication about the comparison between the effects of* $\Delta S°$ *and* $\Delta H°$

(iii) Given that $\Delta G° = \Delta H° - T\Delta S°$ and $\Delta S° < 0$, an increase in temperature causes an increase in the value of $\Delta G°$ ($\Delta G°$ becomes less negative). ***1 pt***

- *One point earned for the description of the effect of an increase in temperature on* $\Delta S°$ *and consequently on* $\Delta G°$
- *No point earned for an argument based on Le Châtelier's principle*

(b) (i) The reaction rate depends on the reaction <u>kinetics</u>, which is determined by the value of the activation energy, E_{act}. If the activation energy is large, a reaction that is thermodynamically spontaneous may proceed very slowly (if at all). ***1 pt***

- *One point earned for linking the rate of the reaction to the activation energy, which may be explained verbally or shown on a reaction profile diagram*

(ii) The catalyst has no effect on the value of $\Delta G°$. ***1 pt***

The catalyst reduces the value of E_{act}, increasing the rate of reaction, but has no effect on the values of $\Delta H°$ and $\Delta S°$, so it cannot affect the thermodynamics of the reaction. ***1 pt***

- *One point earned for indicating no change in the value of* $\Delta G°$
- *One point earned for indicating (verbally, or with a reaction-profile diagram) that the catalyst affects the activation energy*

Excellent Response (8 points)

a) i $\Delta S^{\circ}_{298} < 0$, b/c the reactants go to a less "random" state (ie. 3m' of gas → 1m' of solid + 1m' of liquid)

ii $\boxed{\Delta H_{298}}$ provides the driving force, b/c

the rxn is <u>spontaneous</u> at 298, which means that the $\Delta G^{\circ}_{rxn} < 0$, + since $\Delta G^{\circ} = \underbrace{\Delta H}_{\text{negative}} \underbrace{- T\Delta S}_{\text{positive}}$ the ΔH is more influential in driving the rxn

$\Delta G_{rxn} < 0$

$0 > \Delta H - T\Delta S$

<u>neg</u> of ΔH is $\boxed{\text{more}}$ than <u>positive</u> of $-T\Delta S$

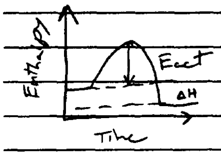
iii If the Temp. was raised, then the ΔG would become less negative + eventually positive (at high enough Temp's), b/c

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

a) iii (cont.) $\Delta G = \Delta H - T\Delta S$ — neg

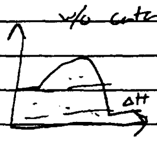
since $\Delta S < 0$, as Temp increases, $-T\Delta S$ increase in the positive direction, therefore ΔG increases in the positive direction

b) i) though the ΔG° might be < 0, the rxn still has to overcome the <u>activation energy</u> which can be very high. This could cause a rxn with a low (< 0) ΔG to proceed slowly.

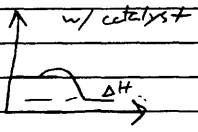


ii. the catalyst has no effect on the ΔG_{rxn} of the reaction, it merely lowers the activation energy, allowing the reaction to proceed more quickly

w/o catalyst



w/ catalyst



$\Delta H = \Delta H$

$\Delta G^{\circ} = \Delta G^{\circ}$ w/ or w/o catalyst

Commentary on Response

A full score of 8 points was earned for this response.

Good Response (7 points)

a) i. ΔS° is negative because the total moles of gas decreases. ~~Since~~ Since gas has the highest entropy, a decrease in gas moles causes a decrease in entropy.

ii. ΔH° is the driving force. Ordinarily, according to the Laws of Thermodynamics, reactions tend toward greater disorder/entropy. But since this reaction decreases entropy, ΔH must drive it in the opposite direction.

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

Since $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, ~~and~~ an increase in T would make the $T\Delta S^\circ$ term more negative and $\Delta H - T\Delta S$ would become greater. Thus, increase in temperature ~~in~~ makes ΔG° bigger.

b) i. Spontaneous reactions merely mean the reaction proceeds in the forward direction automatically. However, it ~~a~~ indicates nothing about the reaction's rate. ~~A spontaneous react~~ A reaction can be spontaneous even if it is extremely slow.

Furthermore, some reactions require an activation energy (E_a) to begin. Without the E_a, they will not react.

ii Catalysts lower the E_a of a reaction. Thus,

Catalysts increase the reaction rate. This increases the ~~amoun~~ amount of free energy released (increases ΔG) because less energy is put into the reaction to get it started. Less input means more free energy will be available.

Commentary on Response

In part (a) ii both points were earned for a correct justification using the Gibbs-Helmholtz equation. A single point was lost for an incorrect statement in part (b) ii regarding the effect of a catalyst on ΔG. The total score for this response was 7 points.

Fair Response (5 points)

(a)(i) Entropy will be negative because you are going from gases to a solid & liquid which is more uniform (opposite of entropy.)

(ii) ΔH because ΔS says that it's not likely to happen.

(b)(i) The reaction will be spontaneous but it could just be very slow kind of like rust.

(iii) [illegible]

(ii) It does not change the amount of free energy given off, it just makes it the reaction produce it faster.

Commentary on Response

This response earned a score of 5 points. Part (a) iii was not addressed and part (b) i was essentially a restatement of the question. One point was earned in part (b) ii for indicating that the free energy change would not change, but the second point was not earned because the effect of a catalyst on E_{act} was not mentioned.

Commentary on Free-Response Question 7

Only about 14 percent of the students chose to answer this question, which dealt with basic topics covered in both the first-year high school chemistry course and the AP course. In part (a) and part (c), the students were asked to demonstrate knowledge of ions and their effect on conductivity and vapor pressure in solutions. Part (b) allowed them to express knowledge of colligative properties and the relationship to freezing-point depression. Part (d) asked the students to understand and communicate about salt hydrolysis. Performance on this question was the weakest among all the free-response questions. The mean score was only 2.7 points (34%).

Errors that were commonly made included stating that C_2H_5OH was a strong base and its solution had the highest pH. Teachers need to make clear to their students that the presence of an OH group in a formula does not always indicate the substance is a strong base. Many students used the terms "insoluble" and "immiscible" to describe why solutions were not good conductors despite the given fact that all four flasks contained 0.1 *M* solutions, hence each contained a soluble substance. A significant number of responses showed a confusion regarding the effect of the volatile solute C_2H_5OH on the vapor pressure of the water above the solution. All too frequently, students misinterpreted the last part of the question, thinking that the highest pH meant the highest H^+ concentration.

In general, the responses indicated that teachers should advise their students to give complete explanations. Quite often students offered reasons such as "organic compounds do not conduct" and "NaF is a basic salt." Students need to provide the reason "why," since such statements of fact are rarely acceptable as explanations. Also, if students are not sure of an answer, it is to their advantage to make a qualified guess even though they may not be sure of the explanation. Finally, teachers should tell students to be as clear as possible when stating their answers and giving explanations, either answering the parts sequentially or making sure that they are plainly labeled.

Scoring Guidelines for Free-Response Question 7

Question 7
(8 points)

(a) C_2H_5OH (Flask #3) ***1 pt***

Ethanol, a nonelectrolyte, does not break up or dissociate in solution. ***1 pt***

- *One point earned for identifying C_2H_5OH*
- *One point earned for the correct explanation.*
- *Explanation point earned for a description of a nonelectrolyte (e.g., something that does not break up or does not dissociate.)*
- *No point earned for describing C_2H_5OH as organic, or as the compound that contains the most hydrogens.*

(b) $MgCl_2$ (Flask #2) ***1 pt***

The freezing-point depression is proportional to the concentration of solute particles. All solutes are at the same concentration, but the van't Hoff factor (i) is largest for $MgCl_2$. ***1 pt***

- *One point earned for identifying $MgCl_2$.*
- *One point earned for the correct explanation.*

(c) C_2H_5OH (Flask #3) ***1 pt***

The lowering of vapor pressure of water is directly proportional to the concentration of solute particles in solution. C_2H_5OH is the only nonelectrolyte, so it will have the fewest solute particles in solution. ***1 pt***

- *One point earned for identifying C_2H_5OH.*
- *One point earned for the correct explanation.*

(d) NaF (Flask #1) ***1 pt***

The F^- ion, generated upon dissolution of NaF, is a weak base. It is the only solution with pH > 7. ***1 pt***

- *One point earned for identifying NaF.*
- *One point earned for the correct explanation.*

Excellent Response (8 points)

a) C_2H_5OH solution will have the lowest electrical conductivity, since it is not an electrolyte; solutions containing ions will conduct electricity the best:
NaF will dissociate into Na^+ and F^- in water, producing ions and allowing current to flow
$MgCl_2$ will dissociate into Mg^{2+} and Cl^-, producing ions
even CH_3COOH will dissociate partially in water to produce H^+ and CH_3COO^- ions
but C_2H_5OH will not dissociate appreciably at all, so little current can flow through such a solution

b) $MgCl_2$ will have the lowest freezing pt; freezing pt depression is directly proportional to the # of "pieces" dissolved in water: C_2H_5OH stays a single unit in water so the concentration of such "pieces" is .10 M.
NaF and CH_3COOH will each dissociate into two ions, so the concentration of the "pieces" in these solutions will be .20 M; each unit of $MgCl_2$ will dissociate into 3 "pieces" → one Mg^{2+} ion and two Cl^- ions; thus the concentration of ions in that solution will be .30 M; therefore, $MgCl_2$ will depress the freezing pt the most out of the four solutes

c) the vapor pressure of water is the greatest above the C_2H_5OH solution; the vapor pressure of water is directly proportional to its mole fraction; taking into account the concept (from part b) - that the other solutes will dissociate into one or more ions, these other solu- will decrease the mole fraction of H_2O much more than C_2H_5OH; since C_2H_5OH decreases the mole fraction of water the least, the mole fraction of water in C_2H_5OH solution is the greatest, thus making its vapor pressure the greatest

d) NaF solution has the highest pH, $MgCl_2$ is a neutral salt, while C_2H_5OH is an alcohol (also neutral); CH_3COOH is a weak acid, NaF will dissociate in H_2O to form F^-, which is the conjuate base of the weak acid HF - the F^- ions will pull protons off of nearby water molecules, decreasing $[H^+]$, increasing $[OH^-]$, and making the solution basic

Commentary on Response

All four answers were correct and in each explanation the student demonstrated understanding of concept involved. Thus this response earned a full score of 8 points.

Good Response (6 points)

a The one with the lowest electrical conductivity will dissociate into the fewest particles: C_2H_5OH

b The one with the lowest freezing point will dissociate into the greatest # of particles: $MgCl_2$. Since the addition of any solute to water will lower the H_2O's freezing point, the solution w/ the greatest # of freezing-point-depressing particles will lower it the most. (In aqueous solution).

c The addition of any solute will lower the vapor pressure of water. Thus, the solution with the fewest dissociated particles -- C_2H_5OH -- will disturb the vapor pressure of water the least.

d The solution w/ the highest pH is the most basic. NaF and $MgCl_2$ are components of strong acids/bases; they are neutral. CH_3COOH is acetic acid. It has a pH<7. The only one left is C_2H_5OH. It is the most basic/it has the highest pH.

Commentary on Response

In this response, which earned a total score of 6 points, the student's error in thinking that NaF is the salt of a strong acid/strong base led to the misidentification of the solution with the highest pH as 0.1 *M* C_2H_5OH.

Fair Response (4 points)

Ⓐ Because electrical conductivity is related to the number of ions in solution, the least conductive is C_2H_5OH, because it dissociates the least.

Ⓑ $MgCl_2$ solution will have the lowest freezing point, because the change in freezing pt is directly related to the van't Hoff factor: $\Delta T_f = K_f \cdot m \cdot i$

$MgCl_2$ provides the most moles in solution, and thus decreases freezing point the most.

Ⓒ The vapor pressure is greatest above NaF, because having the lowest molar mass, at equal M solutions, means it has the fewest grams in solution, giving water the greatest vapor pressure.

(vapor pressure decreases with an increase in amt of solute)

Ⓓ The CH_3COOH has a high pH because of the OH^- that dissociated to create a basic solution.

Commentary on Response

Both part (a) and part (b) earned full credit. No credit was earned in part (c), nor in part (d), in which the student has misidentified acetic acid, CH_3COOH, as a base. The total score for this response was 4 points.

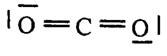
Commentary on Free-Response Question 8

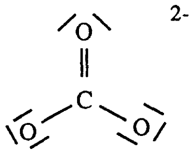
This question, chosen by the great majority of students, required the students to draw and interpret Lewis electron-dot diagrams for some simple non-metal compounds. Half of the 8 points could be earned for drawing the electron-dot diagrams, a basic skill covered in both the first year high school chemistry course and in the AP Chemistry course. The students did well, with a mean score of 4.38 out of 8 points (55%). Overall, the student responses seemed to show a good understanding of Lewis structures but were weaker in their explanation of resonance and polarity due to molecular geometry. Common errors included mistakes in drawing the proper numbers or configurations of electrons in the Lewis structures for CO_3^{2-}, CO_2, or SF_4. Also, many responses showed confusion regarding the distinction between pi bonds and double bonds, or they failed to relate molecular geometry to polarity.

Scoring Guidelines for Free-Response Question 8

Question 8
(8 points)

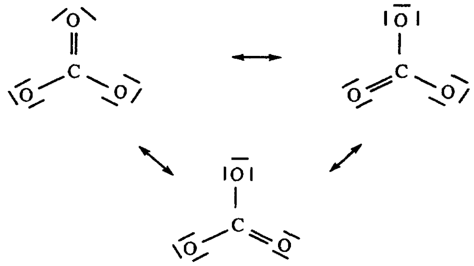
(a) (i) *2 pts*





- *One point earned for each Lewis electron-dot structure*
- *Indication of lone pairs of electrons are required on each structure*
- *Resonance forms of CO_3^{2-} are not required*

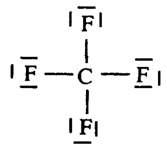
(ii) In CO_2, the C–O interactions are double bonds, **OR**, in CO_3^{2-} the C–O interactions are resonance forms (or figures below.) *1 pt*

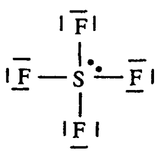


The carbon-oxygen bond length is greater in the resonance forms than in the double bonds. *1 pt*

- *1st point earned for indicating double bonds are present in CO_2 OR resonance occurs in CO_3^{2-}*
- *2nd point earned for **BOTH** of the above **AND** indicating the relative lengths of the bond types*

(b) (i) *2 pts*

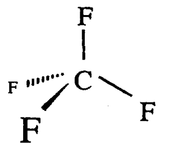


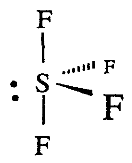


- *One point earned for each Lewis electron-dot structure*
- *Lone pairs of electrons are required on each structure*

(ii) CF_4 has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule. *1 pt*

With five pairs of electrons around the central S atom, SF_4 exhibits a trigonal bipyramidal electronic geometry, with the lone pair of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar. *1 pt*

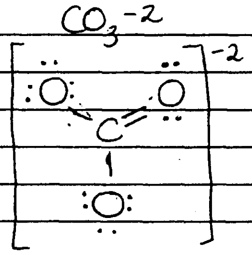




- *One point earned for each molecule for proper geometry and explanation*

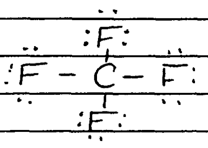
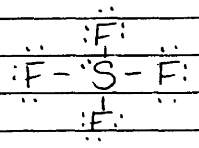
Excellent Response (8 points)

8) (a) [i] CO_2 CO_3^{-2}

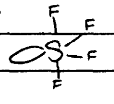



[ii] In the carbonate ion, there is a resonance structure, so that in essence there is 1⅓ bonds between every C-O. However, in the carbon dioxide molecule, there are double bonds between every C-O. These double bonds, involving more electrons are stronger and pull more tightly on the atoms. This brings the atoms closer together and shortens the bond length.

b) [i] CF_4 SF_4

[ii] The CF_4 molecule is tetrahedral; all of the fluorine atoms are equally spaced. Therefore, not one of them attracts more electrons and causes the molecule to be polar. Rather they pull equally and yield a nonpolar molecule. The SF_4 molecule, on the other hand, is in the see-saw shape, with four fluorine atoms on one side of the sufur and an unshared electron pair on the other:



This unequal distribution of charge causes polarity in the molecule.

Commentary on Response

This response shows good understanding of Lewis structures and resonance and the application of these concepts to explain the polarity/nonpolarity of molecules. A full score of 8 points was earned.

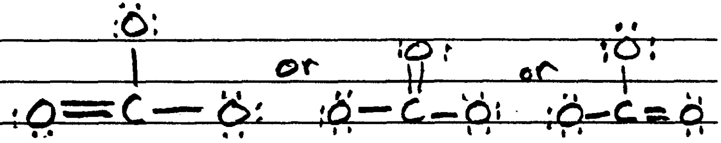
Good Response (6 points)

(a) (i)

CO_2:

4+12= 16e-

CO_3^{2-}:

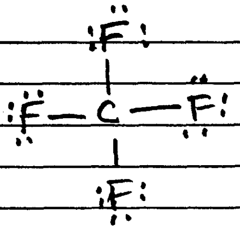


16+6+2= 24e-
18e-

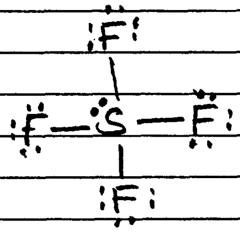
(ii) Since the lewis structure of CO_3^{2-} shows a resonance form the bond length is an average of a double and a single. Since CO_2 has two double bonds its length is shorter than the average between a double and a single.

(b) (i)

CF_4:
32e-
24e-



SF_4:
34e-
26e-



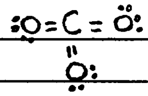
(ii) SF_4 is polar because it has an extra pair of e- on the central atom and the e- pair has more repulsion than the atoms have on eachother. CF_4 is balanced in shape and has no e- pairs coming off of the central atom, all of the atoms have the same force on eachother = symetrical.

Commentary on Response

In this response, which earned a total score of 6 points, the student failed to include the molecular geometry for either molecule in part (b) ii.

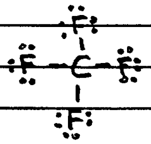
Fair Response (4 points)

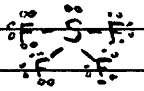
8. (a) (i)



(ii) the carbon-oxygen bond length in CO_3^{-2} is greater than in CO_2 because the added oxygen in CO_3^{-2} has unshared pairs that, when in contact with the unshared pairs from the other two oxygens, repel and created a slightly longer bond length than is required for only the two oxygens of CO_2.

(b) (i)





(ii) The CF_4 molecule has a tetrahedral Shape and a hypridization of Sp_3 that allows the entire molecule to be symetrical and because it has an completely equal pull in every direction, it is therefore nonpolar.

The SF_4 molecule has a DSp_3 hybridization and a square planar shape. SF_4 is polar because of the group of unshared pairs at the top of the molecule that result in an unequal balance of pulling forces throughout the molecule.

Commentary on Response

This response earned a score of 4 points. One point was earned in part (a) i for the correct Lewis structure of CO_2, but no points were earned in part (a) ii, which lacked any reference to resonance in CO_3^{2-} or the double bonds in CO_2. The Lewis structures were correct in part (b) i. However, in part (b) ii, while the geometry of CF_4 was correctly identified, the geometry of SF_4 was not.

AP Chemistry

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