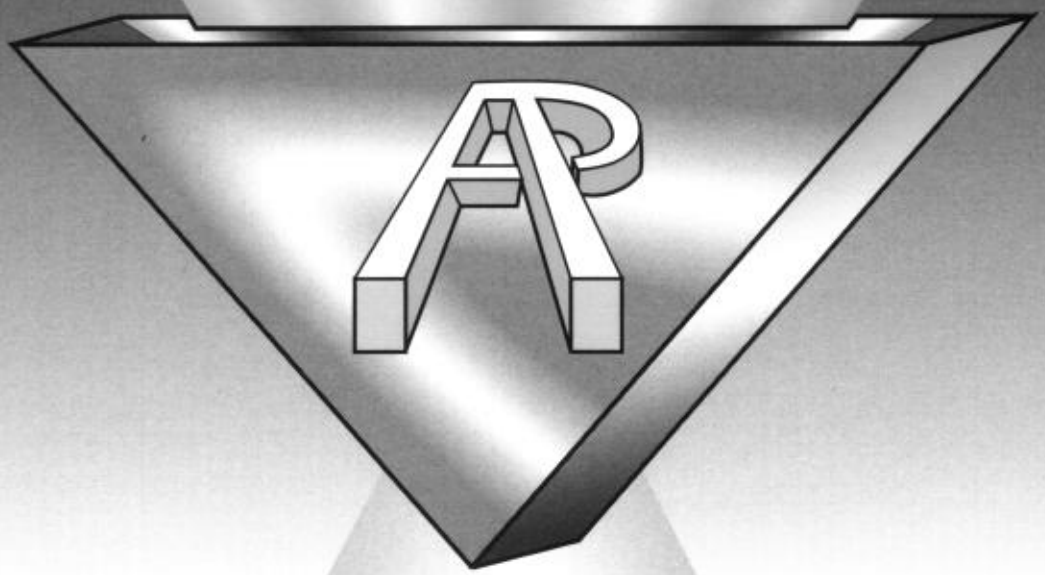


1994 AP® Chemistry: Free-Response Scoring Guide with Multiple-Choice Section

Advanced Placement Program®
THE COLLEGE BOARD

With analysis by Chief Faculty Consultant
Robert W. Gleason

CHEMISTRY

Three hours are allotted for this examination: 1 hour and 30 minutes for Section I, which consists of multiple-choice questions, and 1 hour and 30 minutes for Section II, which consists of problems and essay questions. Section I is printed in this examination booklet; Section II, in a separate booklet.

Battery-operated hand-held calculators may be used in both sections of the examination. All calculator memories must be cleared of both programs and data; no peripheral devices such as magnetic cards or tapes will be allowed. Calculators may not be shared.

SECTION I

Time — 1 hour and 30 minutes

Number of questions — 75

Percent of total grade — 45

This examination contains 75 multiple-choice questions. Therefore, please be careful to fill in only the ovals that are preceded by numbers 1 through 75 on your answer sheet.

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.

CHEMISTRY
SECTION I
Time—1 hour and 30 minutes

Material in the following table may be useful in answering the questions in this section of the examination.

DO NOT DETACH FROM BOOK.

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)

Note: For all questions involving solutions and/or chemical equations, assume that the system is in pure water and at room temperature unless otherwise stated.

Part A

Directions: Each set of lettered choices below refers to the numbered questions or statements immediately following it. Select the one lettered choice that best answers each question or 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

(A) Heisenberg uncertainty principle
(B) Pauli exclusion principle
(C) Hund's rule (principle of maximum multiplicity)
(D) Shielding effect
(E) Wave nature of matter

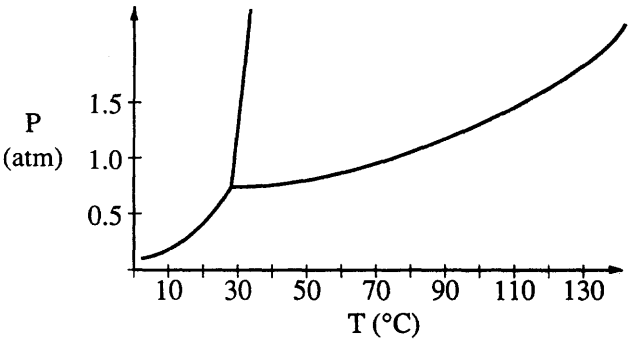
1. Can be used to predict that a gaseous carbon atom in its ground state is paramagnetic

2. Explains the experimental phenomenon of electron diffraction

3. Indicates that an atomic orbital can hold no more than two electrons

4. Predicts that it is impossible to determine simultaneously the exact position and the exact velocity of an electron

Questions 5-7 refer to the phase diagram below of a pure substance.



(A) Sublimation
(B) Condensation
(C) Solvation
(D) Fusion
(E) Freezing

5. If the temperature increases from 10° C to 60° C at a constant pressure of 0.4 atmosphere, which of the processes occurs?

6. If the temperature decreases from 110° C to 40° C at a constant pressure of 1.1 atmospheres, which of the processes occurs?

7. If the pressure increases from 0.5 to 1.5 atmospheres at a constant temperature of 50° C, which of the processes occurs?

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Questions 8-10 refer to the following diatomic species.

(A) Li_2
(B) B_2
(C) N_2
(D) O_2
(E) F_2

8. Has the largest bond-dissociation energy

9. Has a bond order of 2

10. Contains 1 sigma (σ) and 2 pi (π) bonds

Questions 11-13

(A) Pb
(B) Ca
(C) Zn
(D) As
(E) Na

11. Utilized as a coating to protect Fe from corrosion

12. Is added to silicon to enhance its properties as a semiconductor

13. Utilized as a shield from sources of radiation

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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.

14. Which of the following is lower for a 1.0-molar aqueous solution of any solute than it is for pure water?

    (A) pH
    (B) Vapor pressure
    (C) Freezing point
    (D) Electrical conductivity
    (E) Absorption of visible light

15. In a molecule in which the central atom exhibits sp^3d^2 hybrid orbitals, the electron pairs are directed toward the corners of

    (A) a tetrahedron
    (B) a square-based pyramid
    (C) a trigonal bipyramid
    (D) a square
    (E) an octahedron

16. Commercial vinegar was titrated with NaOH solution to determine the content of acetic acid, $HC_2H_3O_2$. For 20.0 milliliters of the vinegar, 26.7 milliliters of 0.600-molar NaOH solution was required. What was the concentration of acetic acid in the vinegar if no other acid was present?

    (A) 1.60 *M*
    (B) 0.800 *M*
    (C) 0.600 *M*
    (D) 0.450 *M*
    (E) 0.200 *M*

17. Relatively slow rates of chemical reaction are associated with which of the following?

    (A) The presence of a catalyst
    (B) High temperature
    (C) High concentration of reactants
    (D) Strong bonds in reactant molecules
    (E) Low activation energy

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18. $2\ H_2O + 4\ MnO_4^- + 3\ ClO_2^- \rightarrow 4\ MnO_2 + 3\ ClO_4^- + 4\ OH^-$

Which species acts as an oxidizing agent in the reaction represented above?

(A) H_2O
(B) ClO_4^-
(C) ClO_2^-
(D) MnO_2
(E) MnO_4^-

19. In which of the following compounds is the mass ratio of chromium to oxygen closest to 1.62 to 1.00 ?

(A) CrO_3
(B) CrO_2
(C) CrO
(D) Cr_2O
(E) Cr_2O_3

20. $\ldots Ag^+ + \ldots AsH_3(g) + \ldots OH^- \rightarrow \ldots Ag(s) + \ldots H_3AsO_3(aq) + \ldots H_2O$

When the equation above is balanced with lowest whole-number coefficients, the coefficient for OH^- is

(A) 2
(B) 4
(C) 5
(D) 6
(E) 7

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21. Correct statements about alpha particles include which of the following?

I. They have a mass number of 4 and a charge of +2.
II. They are more penetrating than beta particles.
III. They are helium nuclei.

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

22. $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

In the equilibrium represented above, the species that act as bases include which of the following?

I. HSO_4^-
II. H_2O
III. SO_4^{2-}

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

23. Step 1: $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

Step 2: $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

Step 3: $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

The proposed steps for a catalyzed reaction between Ce^{4+} and Tl^{+} are represented above. The products of the overall catalyzed reaction are

(A) Ce^{4+} and Tl^{+}
(B) Ce^{3+} and Tl^{3+}
(C) Ce^{3+} and Mn^{3+}
(D) Ce^{3+} and Mn^{4+}
(E) Tl^{3+} and Mn^{2+}

24. A sample of 0.0100 mole of oxygen gas is confined at 37° C and 0.216 atmosphere. What would be the pressure of this sample at 15° C and the same volume?

(A) 0.0876 atm
(B) 0.175 atm
(C) 0.201 atm
(D) 0.233 atm
(E) 0.533 atm

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25. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$ $\quad \Delta H^\circ = -286$ kJ

$2\ Na(s) + \frac{1}{2} O_2(g) \rightarrow Na_2O(s)$ $\quad \Delta H^\circ = -414$ kJ

$Na(s) + \frac{1}{2} O_2(g) + \frac{1}{2} H_2(g) \rightarrow NaOH(s)$ $\quad \Delta H^\circ = -425$ kJ

Based on the information above, what is the standard enthalpy change for the following reaction?

$$Na_2O(s) + H_2O(\ell) \rightarrow 2\ NaOH(s)$$

(A) −1,125 kJ
(B) −978 kJ
(C) −722 kJ
(D) −150 kJ
(E) +275 kJ

26. Which of the following actions would be likely to change the boiling point of a sample of a pure liquid in an open container?

I. Placing it in a smaller container
II. Increasing the number of moles of the liquid in the container
III. Moving the container and liquid to a higher altitude

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

27. Which of the following sets of quantum numbers (n, l, m_ℓ, m_s) best describes the valence electron of highest energy in a ground-state gallium atom (atomic number 31) ?

(A) $4, 0, 0, \frac{1}{2}$

(B) $4, 0, 1, \frac{1}{2}$

(C) $4, 1, 1, \frac{1}{2}$

(D) $4, 1, 2, \frac{1}{2}$

(E) $4, 2, 0, \frac{1}{2}$

GO ON TO THE NEXT PAGE

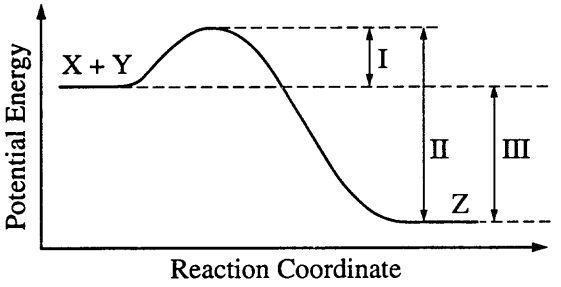
28. Given that a solution is 5 percent sucrose by mass, what additional information is necessary to calculate the molarity of the solution?

I. The density of water
II. The density of the solution
III. The molar mass of sucrose

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

29. When an aqueous solution of NaOH is added to an aqueous solution of potassium dichromate, $K_2Cr_2O_7$, the dichromate ion is converted to

(A) CrO_4^{2-}
(B) CrO_2^-
(C) Cr^{3+}
(D) $Cr_2O_3(s)$
(E) $Cr(OH)_3(s)$



30. The energy diagram for the reaction $X + Y \rightarrow Z$ is shown above. The addition of a catalyst to this reaction would cause a change in which of the indicated energy differences?

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

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31. $H_2C_2O_4 + 2\ H_2O \rightleftarrows 2\ H_3O^+ + C_2O_4^{2-}$

Oxalic acid, $H_2C_2O_4$, is a diprotic acid with $K_1 = 5.36 \times 10^{-2}$ and $K_2 = 5.3 \times 10^{-5}$. For the reaction above, what is the equilibrium constant?

(A) 5.36×10^{-2}
(B) 5.3×10^{-5}
(C) 2.8×10^{-6}
(D) 1.9×10^{-10}
(E) 1.9×10^{-13}

32. CH_3CH_2OH boils at 78° C and CH_3OCH_3 boils at −24° C, although both compounds have the same composition. This difference in boiling points may be attributed to a difference in

(A) molecular mass
(B) density
(C) specific heat
(D) hydrogen bonding
(E) heat of combustion

33. A hydrocarbon gas with an empirical formula CH_2 has a density of 1.88 grams per liter at 0° C and 1.00 atmosphere. A possible formula for the hydrocarbon is

(A) CH_2
(B) C_2H_4
(C) C_3H_6
(D) C_4H_8
(E) C_5H_{10}

34. $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ (*X*) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$ (*Y*) $HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$ (*Z*)

Based on concepts of polarity and hydrogen bonding, which of the following sequences correctly lists the compounds above in the order of their increasing solubility in water?

(A) $Z < Y < X$
(B) $Y < Z < X$
(C) $Y < X < Z$
(D) $X < Z < Y$
(E) $X < Y < Z$

GO ON TO THE NEXT PAGE

35. For which of the following processes would ΔS have a negative value?

I. $2\ Fe_2O_3(s) \rightarrow 4\ Fe(s) + 3\ O_2(g)$

II. $Mg^{2+} + 2\ OH^- \rightarrow Mg(OH)_2(s)$

III. $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$

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

36. $$Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)$$

An electrolytic cell based on the reaction represented above was constructed from zinc and copper half-cells. The observed voltage was found to be 1.00 volt instead of the standard cell potential, E^0, of 1.10 volts. Which of the following could correctly account for this observation?

(A) The copper electrode was larger than the zinc electrode.
(B) The Zn^{2+} electrolyte was $Zn(NO_3)_2$, while the Cu^{2+} electrolyte was $CuSO_4$.
(C) The Zn^{2+} solution was more concentrated than the Cu^{2+} solution.
(D) The solutions in the half-cells had different volumes.
(E) The salt bridge contained KCl as the electrolyte.

37. A sample of 3.30 grams of an ideal gas at 150.0°C and 1.25 atmospheres pressure has a volume of 2.00 liters. What is the molar mass of the gas? The gas constant, R, is 0.0821 (L · atm)/(mol · K).

(A) 0.0218 gram/mole
(B) 16.2 grams/mole
(C) 37.0 grams/mole
(D) 45.8 grams/mole
(E) 71.6 grams/mole

38. Concentrations of colored substances are commonly measured by means of a spectrophotometer. Which of the following would ensure that correct values are obtained for the measured absorbance?

I. There must be enough sample in the tube to cover the entire light path.
II. The instrument must be periodically reset using a standard.
III. The solution must be saturated.

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

39. Samples of F_2 gas and Xe gas are mixed in a container of fixed volume. The initial partial pressure of the F_2 gas is 8.0 atmospheres and that of the Xe gas is 1.7 atmospheres. When all of the Xe gas reacted, forming a solid compound, the pressure of the unreacted F_2 gas was 4.6 atmospheres. The temperature remained constant. What is the formula of the compound?

(A) XeF
(B) XeF_3
(C) XeF_4
(D) XeF_6
(E) XeF_8

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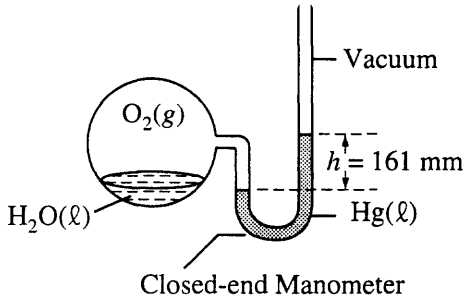

40. The system shown above is at equilibrium at 28° C. At this temperature, the vapor pressure of water is 28 millimeters of mercury. The partial pressure of $O_2(g)$ in the system is

(A) 28 mm Hg
(B) 56 mm Hg
(C) 133 mm Hg
(D) 161 mm Hg
(E) 189 mm Hg

41. A strip of metallic scandium, Sc, is placed in a beaker containing concentrated nitric acid. A brown gas rapidly forms, the scandium disappears, and the resulting liquid is brown-yellow but becomes colorless when warmed. These observations best support which of the following statements?

(A) Nitric acid is a strong acid.
(B) In solution scandium nitrate is yellow and scandium chloride is colorless.
(C) Nitric acid reacts with metals to form hydrogen.
(D) Scandium reacts with nitric acid to form a brown gas.
(E) Scandium and nitric acid react in mole proportions of 1 to 3.

42.

Mass of an empty container	3.0 grams
Mass of the container plus the solid sample	25.0 grams
Volume of the solid sample	11.0 cubic centimeters

The data above were gathered in order to determine the density of an unknown solid. The density of the sample should be reported as

(A) 0.5 g/cm^3
(B) 0.50 g/cm^3
(C) 2.0 g/cm^3
(D) 2.00 g/cm^3
(E) 2.27 g/cm^3

43. Which of the following pairs of compounds are isomers?

(A) $CH_3—CH_2—CH_2—CH_3$ and $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

(B) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ and $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

(C) $CH_3—O—CH_3$ and $CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$

(D) $CH_3—OH$ and $CH_3—CH_2—OH$

(E) CH_4 and $CH_2=CH_2$

44. Which of the following solutions has the lowest freezing point?

(A) 0.20 *m* $C_6H_{12}O_6$, glucose
(B) 0.20 *m* NH_4Br
(C) 0.20 *m* $ZnSO_4$
(D) 0.20 *m* $KMnO_4$
(E) 0.20 *m* $MgCl_2$

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45. A sample of an ideal gas is cooled from 50.0° C to 25.0° C in a sealed container of constant volume. Which of the following values for the gas will decrease?

I. The average molecular mass of the gas
II. The average distance between the molecules
III. The average speed of the molecules

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

46. Which of the following solids dissolves in water to form a colorless solution?

(A) $CrCl_3$
(B) $FeCl_3$
(C) $CoCl_2$
(D) $CuCl_2$
(E) $ZnCl_2$

47. Which of the following has the lowest conductivity?

(A) 0.1 *M* $CuSO_4$
(B) 0.1 *M* KOH
(C) 0.1 *M* $BaCl_2$
(D) 0.1 *M* HF
(E) 0.1 *M* HNO_3

48. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) + \text{energy}$

Some PCl_3 and Cl_2 are mixed in a container at 200° C and the system reaches equilibrium according to the equation above. Which of the following causes an increase in the number of moles of PCl_5 present at equilibrium?

I. Decreasing the volume of the container
II. Raising the temperature
III. Adding a mole of He gas at constant volume

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

49. The isomerization of cyclopropane to propylene is a first-order process with a half-life of 19 minutes at 500° C. The time it takes for the partial pressure of cyclopropane to decrease from 1.0 atmosphere to 0.125 atmosphere at 500° C is closest to

(A) 38 minutes
(B) 57 minutes
(C) 76 minutes
(D) 152 minutes
(E) 190 minutes

50. Which of the following acids can be oxidized to form a stronger acid?

(A) H_3PO_4
(B) HNO_3
(C) H_2CO_3
(D) H_3BO_3
(E) H_2SO_3

51. $4\ HCl(g) + O_2(g) \rightleftarrows 2\ Cl_2(g) + 2\ H_2O(g)$

Equal numbers of moles of HCl and O_2 in a closed system are allowed to reach equilibrium as represented by the equation above. Which of the following must be true at equilibrium?

I. [HCl] must be less than $[Cl_2]$.
II. $[O_2]$ must be greater than [HCl].
III. $[Cl_2]$ must equal $[H_2O]$.

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

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52. When dilute nitric acid was added to a solution of one of the following chemicals, a gas was evolved. This gas turned a drop of limewater, $Ca(OH)_2$, cloudy, due to the formation of a white precipitate. The chemical was

(A) household ammonia, NH_3
(B) baking soda, $NaHCO_3$
(C) table salt, NaCl
(D) epsom salts, $MgSO_4 \cdot 7H_2O$
(E) bleach, 5% NaOCl

53. If 87 grams of K_2SO_4 (molar mass 174 grams) is dissolved in enough water to make 250 milliliters of solution, what are the concentrations of the potassium and the sulfate ions?

	$[K^+]$	$[SO_4^{2-}]$
(A)	0.020 *M*	0.020 *M*
(B)	1.0 *M*	2.0 *M*
(C)	2.0 *M*	1.0 *M*
(D)	2.0 *M*	2.0 *M*
(E)	4.0 *M*	2.0 *M*

54. All of the following statements concerning the characteristics of the halogens are true EXCEPT:

(A) The first ionization energies (potentials) decrease as the atomic numbers of the halogens increase.
(B) Fluorine is the best oxidizing agent.
(C) Fluorine atoms have the smallest radii.
(D) Iodine liberates free bromine from a solution of bromide ion.
(E) Fluorine is the most electronegative of the halogens.

55. What volume of 0.150-molar HCl is required to neutralize 25.0 milliliters of 0.120-molar $Ba(OH)_2$?

(A) 20.0 mL
(B) 30.0 mL
(C) 40.0 mL
(D) 60.0 mL
(E) 80.0 mL

56. It is suggested that SO_2 (molar mass 64 grams), which contributes to acid rain, could be removed from a stream of waste gases by bubbling the gases through 0.25-molar KOH, thereby producing K_2SO_3. What is the maximum mass of SO_2 that could be removed by 1,000. liters of the KOH solution?

(A) 4.0 kg
(B) 8.0 kg
(C) 16 kg
(D) 20. kg
(E) 40. kg

57. Molecules that have planar configurations include which of the following?

I. BCl_3
II. $CHCl_3$
III. NCl_3

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

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

The reaction indicated above is thermodynamically spontaneous at 298 K, but becomes nonspontaneous at higher temperatures. Which of the following is true at 298 K ?

(A) ΔG, ΔH, and ΔS are all positive.
(B) ΔG, ΔH, and ΔS are all negative.
(C) ΔG and ΔH are negative, but ΔS is positive.
(D) ΔG and ΔS are negative, but ΔH is positive.
(E) ΔG and ΔH are positive, but ΔS is negative.

GO ON TO THE NEXT PAGE

59. When a 1.00-gram sample of limestone was dissolved in acid, 0.38 gram of CO_2 was generated. If the rock contained no carbonate other than $CaCO_3$, what was the percent of $CaCO_3$ by mass in the limestone?

(A) 17%
(B) 51%
(C) 64%
(D) 86%
(E) 100%

60. $$I_2(g) + 3\ Cl_2(g) \rightarrow 2\ ICl_3(g)$$

According to the data in the table below, what is the value of $\Delta H°$ for the reaction represented above?

Bond	Average Bond Energy (kilojoules/mole)
I—I	149
Cl—Cl	239
I—Cl	208

(A) −860 kJ
(B) −382 kJ
(C) +180 kJ
(D) +450 kJ
(E) +1,248 kJ

61. A 1-molar solution of which of the following salts has the highest pH ?

(A) $NaNO_3$
(B) Na_2CO_3
(C) NH_4Cl
(D) $NaHSO_4$
(E) Na_2SO_4

62. The electron-dot structure (Lewis structure) for which of the following molecules would have two unshared pairs of electrons on the central atom?

(A) H_2S
(B) NH_3
(C) CH_4
(D) HCN
(E) CO_2

63. What is the maximum mass of copper that could be plated out by electrolyzing aqueous $CuCl_2$ for 16.0 hours at a constant current of 3.00 amperes? (1 faraday = 96,500 coulombs)

(A) 28 grams
(B) 57 grams
(C) 64 grams
(D) 114 grams
(E) 128 grams

64. At 25° C, a sample of NH_3 (molar mass 17 grams) effuses at the rate of 0.050 mole per minute. Under the same conditions, which of the following gases effuses at approximately one-half that rate?

(A) O_2 (molar mass 32 grams)
(B) He (molar mass 4.0 grams)
(C) CO_2 (molar mass 44 grams)
(D) Cl_2 (molar mass 71 grams)
(E) CH_4 (molar mass 16 grams)

65. Barium sulfate is LEAST soluble in a 0.01-molar solution of which of the following?

(A) $Al_2(SO_4)_3$
(B) $(NH_4)_2SO_4$
(C) Na_2SO_4
(D) NH_3
(E) $BaCl_2$

66. What is the pH of a 1.0×10^{-2}-molar solution of HCN ? (For HCN, $K_a = 4.0 \times 10^{-10}$.)

(A) 10
(B) Between 7 and 10
(C) 7
(D) Between 4 and 7
(E) 4

GO ON TO THE NEXT PAGE

67. Substances X and Y that were in a solution were separated in the laboratory using the technique of fractional crystallization. This fractional crystallization is possible because substances X and Y have different

(A) boiling points
(B) melting points
(C) densities
(D) crystal colors
(E) solubilities

68. Which of the following molecules has a dipole moment of zero?

(A) C_6H_6 (benzene)
(B) NO
(C) SO_2
(D) NH_3
(E) H_2S

69. Correct procedures for a titration include which of the following?

I. Draining a pipet by touching the tip to the side of the container used for the titration
II. Rinsing the buret with distilled water just before filling it with the liquid to be titrated
III. Swirling the solution frequently during the titration

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

70. To determine the molar mass of a solid monoprotic acid, a student titrated a weighed sample of the acid with standardized aqueous NaOH. Which of the following could explain why the student obtained a molar mass that was too large?

I. Failure to rinse all acid from the weighing paper into the titration vessel
II. Addition of more water than was needed to dissolve the acid
III. Addition of some base beyond the equivalence point

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

71. $\ldots Fe(OH)_2 + \ldots O_2 + \ldots H_2O \rightarrow \ldots Fe(OH)_3$

If 1 mole of O_2 oxidizes $Fe(OH)_2$ according to the reaction represented above, how many moles of $Fe(OH)_3$ can be formed?

(A) 2
(B) 3
(C) 4
(D) 5
(E) 6

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72. The nuclide $^{249}_{96}Cm$ is radioactive and decays by the loss of one beta (β^-) particle. The product nuclide is

(A) $^{245}_{94}Pu$

(B) $^{245}_{95}Am$

(C) $^{248}_{96}Cm$

(D) $^{250}_{96}Cm$

(E) $^{249}_{97}Bk$

73. $$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

When 0.40 mole of SO_2 and 0.60 mole of O_2 are placed in an evacuated 1.00-liter flask, the reaction represented above occurs. After the reactants and the product reach equilibrium and the initial temperature is restored, the flask is found to contain 0.30 mole of SO_3. Based on these results, the equilibrium constant, K_c, for the reaction is

(A) 20.
(B) 10.
(C) 6.7
(D) 2.0
(E) 1.2

74. A solution of calcium hypochlorite, a common additive to swimming-pool water, is

(A) basic because of the hydrolysis of the OCl^- ion
(B) basic because $Ca(OH)_2$ is a weak and insoluble base
(C) neutral if the concentration is kept below 0.1 molar
(D) acidic because of the hydrolysis of the Ca^{2+} ions
(E) acidic because the acid HOCl is formed

75. A direct-current power supply of low voltage (less than 10 volts) has lost the markings that indicate which output terminal is positive and which is negative. A chemist suggests that the power supply terminals be connected to a pair of platinum electrodes that dip into 0.1-molar KI solution. Which of the following correctly identifies the polarities of the power supply terminals?

(A) A gas will be evolved only at the positive electrode.
(B) A gas will be evolved only at the negative electrode.
(C) A brown color will appear in the solution near the negative electrode.
(D) A metal will be deposited on the positive electrode.
(E) None of the methods above will identify the polarities of the power supply terminals.

STOP

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.

■ REVISED QUANTITATIVE ITEMS FROM THE 1994 CHEMISTRY EXAM

There were a total of 20 quantitative questions in the multiple-choice section of the 1994 AP Chemistry Exam. Below are 10 quantitative questions from this group rewritten to conform to the new format being introduced in 1996, in which calculators will not be allowed for the multiple-choice questions. (The capital "R" following the question number indicates that it is a Revised question.) The remaining quantitative questions from the 1994 exam are those for which students would not typically need a calculator, and therefore represent quantitative questions that would appear exactly as they are now on the new format of the exam.

16R. Commercial vinegar was titrated with NaOH solution to determine the content of acetic acid, $HC_2H_3O_2$. For 20.0 milliliters of the vinegar, 32.0 milliliters of 0.500-molar NaOH solution was required. What was the concentration of acetic acid in the vinegar if no other acid was present?

(A) 1.60 *M*
(B) 0.800 *M*
(C) 0.640 *M*
(D) 0.600 *M*
(E) 0.400 *M*

19R. In which of the following compounds is the mass ratio of chromium to oxygen closest to 1.6 to 1.0?

(A) CrO_3
(B) CrO_2
(C) CrO
(D) Cr_2O
(E) Cr_2O_3

24R. A sample of 0.010 mole of oxygen gas is confined at 127°C and 0.80 atmosphere. What would be the pressure of this sample at 27°C and the same volume?

(A) 0.10 atm
(B) 0.20 atm
(C) 0.60 atm
(D) 0.80 atm
(E) 1.1 atm

25R. $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(\ell)$ $\Delta H^0 = x$

$2\ Na(s) + 1/2\ O_2(g) \rightarrow Na_2O(s)$ $\Delta H^0 = y$

$Na(s) + 1/2\ O_2(g) + 1/2\ H_2(g) \rightarrow NaOH(s)$ $\Delta H^0 = z$

Based on the information above, what is the standard enthalpy change for the following reaction?

$$Na_2O(s) + H_2O(\ell) \rightarrow 2\ NaOH(s)$$

(A) $x + y + z$
(B) $x + y - z$
(C) $x + y - 2z$
(D) $2z - x - y$
(E) $z - x - y$

31R. $H_2C_2O_4 + 2\ H_2O \rightleftharpoons 2\ H_3O^+ + C_2O_4^{2-}$

Oxalic acid, $H_2C_2O_4$, is a diprotic acid with $K_1 = 5 \times 10^{-2}$ and $K_2 = 5 \times 10^{-5}$. Which of the following is equal to the equilibrium constant for the reaction represented above?

(A) 5×10^{-2}
(B) 5×10^{-5}
(C) 2.5×10^{-6}
(D) 5×10^{-7}
(E) 2.5×10^{-8}

37R. A sample of 3.0 grams of an ideal gas at 127°C and 1.0 atmosphere pressure has a volume of 1.5 liters. Which of the following expressions is correct for the molar mass of the gas? The ideal gas constant, R, is 0.08 (L· atm)/(mole·K).

(A) $\dfrac{(0.08)(400)}{(3.0)(1.0)(1.5)}$

(B) $\dfrac{(1.0)(1.5)}{(3.0)(0.08)(400)}$

(C) $\dfrac{(0.08)(1.0)(1.5)}{(3.0)(400)}$

(D) $\dfrac{(3.0)(0.08)(400)}{(1.0)(1.5)}$

(E) $\dfrac{(3.0)(0.08)(1.5)}{(1.0)(400)}$

59R. When a 1.25-gram sample of limestone was dissolved in acid, 0.44 gram of CO_2 was generated. If the rock contained no carbonate other than $CaCO_3$, what was the percent of $CaCO_3$ by mass in the limestone?

(A) 35%
(B) 44%
(C) 67%
(D) 80%
(E) 100%

60R. $I_2(g) + 3\ Cl_2(g) \rightarrow 2\ ICl_3(g)$

According to the data in the table below, what is the value of ΔH^0 for the reaction represented above?

Bond	Average Bond Energy (kilojoules/mole)
I - I	150
Cl - Cl	240
I - Cl	210

(A) - 870 kJ
(B) - 390 kJ
(C) + 180 kJ
(D) + 450 kJ
(E) +1,260 kJ

63R. Which of the following expressions is correct for the maximum mass of copper, in grams, that could be plated out by electrolyzing aqueous $CuCl_2$ for 16 hours at a constant current of 3.0 amperes? (1 faraday = 96,500 coulombs)

(A) $\dfrac{(16)(3{,}600)(3.0)(63.55)(2)}{(96{,}500)}$

(B) $\dfrac{(16)(3{,}600)(3.0)(63.55)}{(96{,}500)(2)}$

(C) $\dfrac{(16)(3{,}600)(3.0)(63.55)}{(96{,}500)}$

(D) $\dfrac{(16)(60)(3.0)(96{,}500)(2)}{(63.55)}$

(E) $\dfrac{(16)(60)(3.0)(96{,}500)}{(63.55)(2)}$

73R. $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

When 0.40 mole of SO_2 and 0.60 mole of O_2 are placed in an evacuated 1.00-liter flask, the reaction represented above occurs. After the reactants and the product reach equilibrium and the initial temperature is restored, the flask is found to contain 0.30 mole of SO_3. Based on these results, the expression for the equilibrium constant, K_c, of the reaction is

(A) $\dfrac{(0.30)^2}{(0.45)(0.10)^2}$

(B) $\dfrac{(0.30)^2}{(0.60)(0.40)^2}$

(C) $\dfrac{(2 \times 0.30)}{(0.45)(2 \times 0.10)}$

(D) $\dfrac{(0.30)}{(0.45)(0.10)}$

(E) $\dfrac{(0.30)}{(0.60)(0.40)}$

Answers to Revised Questions
16R. B
19R. B
24R. C
25R. D
31R. C
37R. D
59R. D
60R. B
63R. B
73R. A

CHEMISTRY

SECTION II

Time—1 hour and 30 minutes

Percent of total grade—55

Parts A, B, and C: Suggested time—50 minutes

Part D: Suggested time—40 minutes

General Instructions

The suggested times will not be announced, and you may proceed freely from one question to the next. Do not spend too long on any one problem.

Pages containing a periodic table and the electrochemical series are printed on 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.

When you are told to begin, open your booklet, carefully tear out the green insert, and start work. The questions are also printed in your essay booklet, but it may be easier to work from the insert when answering questions. Write all your answers in the pink essay booklet. Number your answers as the questions are numbered in the examination book.

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

DO NOT DETACH FROM BOOK.

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)

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

Universal gas constant: $R = 8.31$ joules/(mole · K) $= 0.0821$ liter-atm/(mole · K)
$= 62.4$ liter-mm Hg/(mole · K) $= 1.99$ calories/(mole · K)
$= 8.31$ (volt)(coulombs)/(mole · K)

1 faraday ($\mathcal{F}$) = 96,500 coulombs = 23.060 calories/volt = 96,500 joules/volt

1 calorie = 4.184 joules

1 electron volt/atom = 23.1 kilocalories/mole = 96.5 kilojoules/mole

Speed of light in vacuum = 2.998×10^8 m/sec

$\ln_e = 2.303 \log_{10}$

Planck's constant $h = 6.63 \times 10^{-34}$ joule · sec

Boltzmann's constant $k = 1.38 \times 10^{-23}$ joule/K

Avogadro's number = 6.022×10^{23} molecules/mole

At 25° C, $\frac{RT}{n\mathcal{F}} \ln Q = \frac{0.0591}{n} \log Q$

STANDARD REDUCTION POTENTIALS, E^0, IN WATER SOLUTION AT 25° C (in V)

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

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CHEMISTRY

SECTION II

Time—1 hour and 30 minutes

The percentages given for the parts represent the score weightings for this section of the examination. Spend about 50 minutes on Parts A, B, and C combined and about 40 minutes on Part D.

THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS MUST BE SHOWN CLEARLY. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write your answers in the space provided following each question.

Data necessary for the solution of the problems may be found in the tables on the preceding pages.

Part A

(20 percent)

Solve the following problem.

1. $$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^-(aq)$$

In a saturated solution of MgF_2 at 18° C, the concentration of Mg^{2+} is 1.21×10^{-3} molar. The equilibrium is represented by the equation above.

(a) Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18° C.

(b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 liter of saturated MgF_2 solution at 18° C to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.

(c) Predict whether a precipitate of MgF_2 will form when 100.0 milliliters of a 3.00×10^{-3}-molar $Mg(NO_3)_2$ solution is mixed with 200.0 milliliters of a 2.00×10^{-3}-molar NaF solution at 18° C. Calculations to support your prediction must be shown.

(d) At 27° C the concentration of Mg^{2+} in a saturated solution of MgF_2 is 1.17×10^{-3} molar. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

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Part B

(20 percent)

Solve EITHER problem 2 OR problem 3 in this part. (A second problem will not be scored.)

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

Experiments were conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L) [NO]	[H_2]	Initial Rate of Formation of N_2 (mol/L·min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a) (i) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

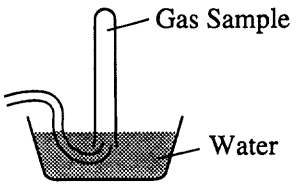
(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. $NO + NO \rightleftharpoons N_2O_2$
II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$
III. $N_2O + H_2 \rightarrow N_2 + H_2O$

Based on the data presented, which of the above is the rate-determining step? Show that the mechanism is consistent with

(i) the observed rate law for the reaction, and
(ii) the overall stoichiometry of the reaction.

GO ON TO THE NEXT PAGE



3. A student collected a sample of hydrogen gas by the displacement of water as shown by the diagram above. The relevant data are given in the following table.

GAS SAMPLE DATA	
Volume of sample	90.0 mL
Temperature	25° C
Atmospheric Pressure	745 mm Hg
Equilibrium Vapor Pressure of H_2O (25° C)	23.8 mm Hg

(a) Calculate the number of moles of hydrogen gas collected.

(b) Calculate the number of molecules of water vapor in the sample of gas.

(c) Calculate the ratio of the average speed of the hydrogen molecules to the average speed of the water vapor molecules in the sample.

(d) Which of the two gases, H_2 or H_2O, deviates more from ideal behavior? Explain your answer.

GO ON TO THE NEXT PAGE

Part C

(15 percent)

4. Answer FIVE of the eight options in this part. (Answers to more than five options will not be scored.)

Give the formulas to show the reactants and the products for FIVE of the following chemical reactions. Each of the reactions occurs in aqueous solution unless otherwise indicated. Represent substances in solution as ions if the substance is extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. In all cases a reaction occurs. You need not balance.

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

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

(a) Excess sodium cyanide solution is added to a solution of silver nitrate.

(b) Solutions of manganese(II) sulfate and ammonium sulfide are mixed.

(c) Phosphorus(V) oxide powder is sprinkled over distilled water.

(d) Solid ammonium carbonate is heated.

(e) Carbon dioxide gas is bubbled through a concentrated solution of potassium hydroxide.

(f) A concentrated solution of hydrochloric acid is added to solid potassium permanganate.

(g) A small piece of sodium metal is added to distilled water.

(h) A solution of potassium dichromate is added to an acidified solution of iron(II) chloride.

GO ON TO THE NEXT PAGE

Part D

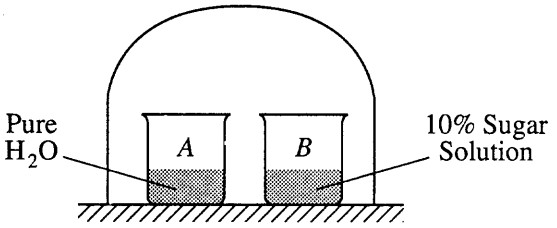
(45 percent)

Spend about 40 minutes on this part of the examination. Answering these questions provides an opportunity to demonstrate your ability to present your material in logical, coherent, and convincing English. Your responses will be judged on the basis of accuracy and importance of the detail cited and on the appropriateness of the descriptive material used. Specific answers are preferable to broad, diffuse responses. Illustrative examples and equations may be helpful.

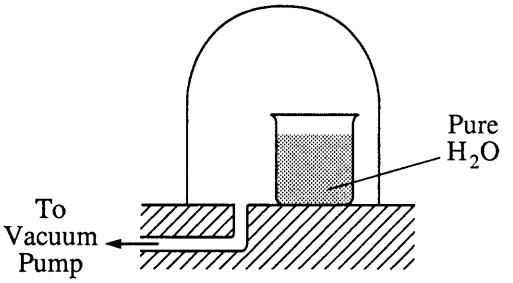
ANSWER THE FOLLOWING ESSAY QUESTION.

5. Discuss the following phenomena in terms of the chemical and physical properties of the substances involved and general principles of chemical and physical change.

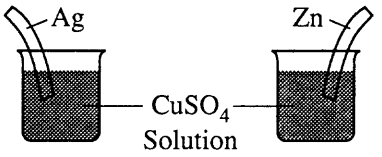
(a) As the system shown on the right approaches equilibrium, what change occurs to the volume of water in beaker A ? What happens to the concentration of the sugar solution in beaker B ? Explain why these changes occur.



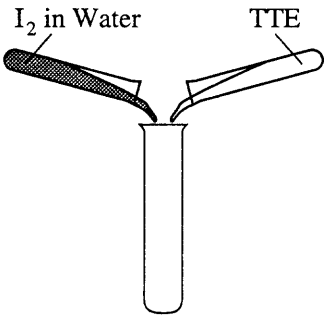
(b) A bell jar connected to a vacuum pump is shown on the right. As the air pressure under the bell jar decreases, what behavior of water in the beaker will be observed? Explain why this occurs.



(c) What will be observed on the surfaces of zinc and silver strips shortly after they are placed in separate solutions of $CuSO_4$, as shown on the right? Account for these observations.



(d) A water solution of I_2 is shaken with an equal volume of a nonpolar solvent such as TTE (trichlorotrifluoroethane). Describe the appearance of this system after shaking. (A diagram may be helpful.) Account for this observation.



GO ON TO THE NEXT PAGE

SELECT TWO OF THE FOUR ESSAY QUESTIONS, NUMBERED 6 THROUGH 9.
(Additional essays will not be scored.)

6. $$2\ H_2S(g) + SO_2(g) \rightleftharpoons 3\ S(s) + 2\ H_2O(g)$$

At 298 K, the standard enthalpy change, $\triangle H°$, for the reaction represented above is −145 kilojoules.

(a) Predict the sign of the standard entropy change, $\triangle S°$, for the reaction. Explain the basis for your prediction.

(b) At 298 K, the forward reaction (i.e., toward the right) is spontaneous. What change, if any, would occur in the value of $\triangle G°$ for this reaction as the temperature is increased? Explain your reasoning using thermodynamic principles.

(c) What change, if any, would occur in the value of the equilibrium constant, K_{eq}, for the situation described in (b)? Explain your reasoning.

(d) The absolute temperature at which the forward reaction becomes nonspontaneous can be predicted. Write the equation that is used to make the prediction. Why does this equation predict only an approximate value for the temperature?

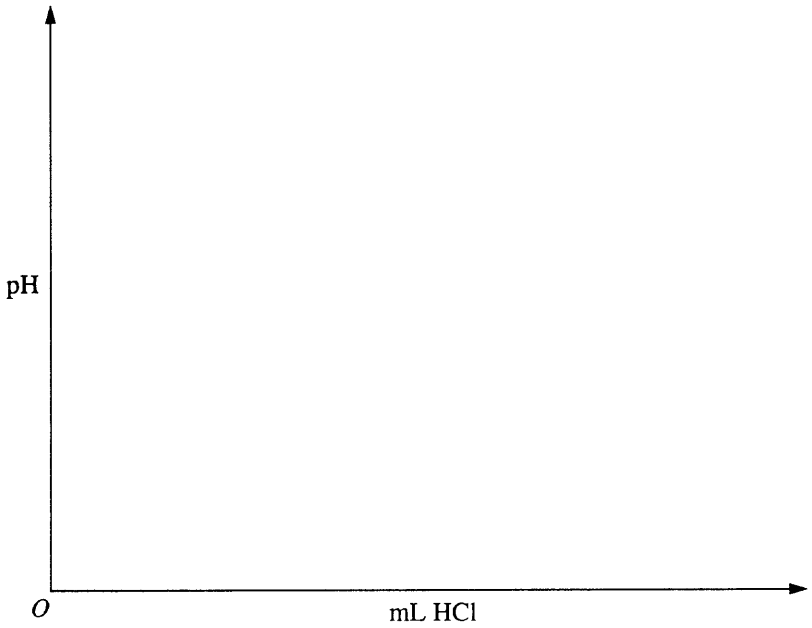
GO ON TO THE NEXT PAGE

7. A chemical reaction occurs when 100. milliliters of 0.200-molar HCl is added dropwise to 100. milliliters of 0.100-molar Na_3PO_4 solution.

(a) Write the two net ionic equations for the formation of the major products.

(b) Identify the species that acts as both a Brönsted acid and as a Brönsted base in the equations in (a). Draw the Lewis electron-dot diagram for this species.

(c) Sketch a graph using the axes provided, showing the shape of the titration curve that results when 100. milliliters of the HCl solution is added slowly from a buret to the Na_3PO_4 solution. Account for the shape of the curve.



(d) Write the equation for the reaction that occurs if a few additional milliliters of the HCl solution are added to the solution resulting from the titration in (c).

GO ON TO THE NEXT PAGE

8. For each of the following, use appropriate chemical principles to explain the observation.

   (a) Sodium chloride may be spread on an icy sidewalk in order to melt the ice; equimolar amounts of calcium chloride are even more effective.

   (b) At room temperature, NH_3 is a gas and H_2O is a liquid, even though NH_3 has a molar mass of 17 grams and H_2O has a molar mass of 18 grams.

   (c) C (graphite) is used as a lubricant, whereas C (diamond) is used as an abrasive.

   (d) Pouring vinegar onto the white residue inside a kettle used for boiling water results in a fizzing/bubbling phenomenon.

GO ON TO THE NEXT PAGE

9. Use principles of atomic structure and/or chemical bonding to answer each of the following.

(a) The radius of the Ca atom is 0.197 nanometer; the radius of the Ca^{2+} ion is 0.099 nanometer. Account for this difference.

(b) The lattice energy of $CaO(s)$ is $-3{,}460$ kilojoules per mole; the lattice energy for $K_2O(s)$ is $-2{,}240$ kilojoules per mole. Account for this difference.

	Ionization Energy (kJ/mol)	
	First	Second
K	419	3,050
Ca	590	1,140

(c) Explain the difference between Ca and K in regard to

(i) their first ionization energies,
(ii) their second ionization energies.

(d) The first ionization energy of Mg is 738 kilojoules per mole and that of Al is 578 kilojoules per mole. Account for this difference.

END OF EXAMINATION

Chapter III

Answers to the 1994 AP Chemistry Examination

■ SECTION I: MULTIPLE-CHOICE

Listed below are the correct answers to the multiple-choice questions and the percentage of AP candidates who attempted each question and answered it correctly. As a general rule, candidates who correctly answered an individual question in this section also achieved a higher mean score on the test as a whole than candidates who did not answer that question correctly. An answer sheet gridded with the correct responses appears on the next page.

Section I Answer Key and Percent Answering Correctly

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

PLACE AP™ NUMBER LABEL HERE.

A. SIGNATURE

To maintain the security of the exam and the validity of my AP grade, I will allow no one other than myself to see the multiple-choice questions and will seal the appropriate section when asked to do so. In addition, I am aware of and agree to the Program's policies and procedures as outlined in the 1994 *AP Bulletin for Students and Parents.*

Sign your name as it will appear on your college applications.

SIDE 1

ETS USE ONLY

	PT1	PT2	PT3	PT4	TOT	EQ	TA1	TA2
FS								
W								
R								

B. YOUR AP NUMBER

C. NAME Omit spaces, hyphens, apostrophes, Jr. or II.

Last Name - first 15 letters | First Name - first 12 letters | MI

D. ADMIN. DAY IN MAY

E. TIME OF DAY

6 AM, 7 AM, 8 AM, 9 AM, 10 AM, 11 AM, 12 PM, 1 PM, 2 PM, 3 PM, 4 PM, 5 PM

ETS USE ONLY

F. AP EXAMINATION(S) TO BE TAKEN USING THIS ANSWER SHEET

Print examination name: CHEMISTRY

Fill in the appropriate oval below for examination name and number.

07 U.S. History	36 Eng. Language & Comp.	66 Math.: Calculus AB
13 Art: History of	37 Eng. Literature & Comp.	68 Math.: Calculus BC
14 Art: Studio Drawing	43 European History	75 Music Theory
15 Art: Studio General	48 French Language	78 Physics B
20 Biology	51 French Literature	80 Physics C: **Mech.**
25 ● Chemistry	55 German Language	80 Physics C: **E & M**
31 Computer Science A	57 Gov. & Pol.: **U.S.**	85 Psychology
33 Computer Science AB	58 Gov. & Pol.: **Comp.**	87 Spanish Language
34 Economics: **Micro**	60 Latin: Vergil	89 Spanish Literature
35 Economics: **Macro**	60 Latin Literature	

G. What language do you know best?

- English
- English and another language about the same
- Another language

H. DO NOT COMPLETE THIS SECTION UNLESS INSTRUCTED TO DO SO.

H1. Essay Choices
Fill in the ovals under the numbers of the essay questions you answered in this examination.

1 2 3 4 5 6
7 8 9 10 11 12

H2. If this answer sheet is for the French Language, French Literature, German Language, Spanish Language, or Spanish Literature Examination, please answer the following questions. (Your responses will not affect your grade.)

1. Have you lived or studied for one month or more in a country where the language of the exam you are now taking is spoken? Yes No
2. Do you regularly speak or hear the language at home? Yes No

SCHOOL USE ONLY

Fee Reduction Granted

Report to Teachers Section Designation 1 2 3 4 5 6 7 8 9

BE SURE EACH MARK IS DARK AND COMPLETELY FILLS THE INTENDED SPACE. IF A QUESTION HAS ONLY FOUR ANSWER OPTIONS, DO NOT MARK THE OPTION E.

Questions 1–135 (A B C D E)

Advanced Placement Program®
THE COLLEGE BOARD
Master ID/Answer Sheet (MIDAS) for May 1994 Form 3QBP

I.N. 201635 18002 • 00657 • DY103P945 Q2664-06 CHW93280

■ SECTION II: FREE-RESPONSE

Report of the Chief Faculty Consultant

Robert W. Gleason
Middlebury College

Grading the Examination

The free-response section of the AP Chemistry Examination is read and scored by faculty consultants — AP Chemistry teachers and college chemistry professors — who are under the direction of a chemistry teacher designated as the chief faculty consultant. The faculty consultants are from secondary schools and colleges throughout the United States, and also from Canada. The faculty consultants do not have access to, and therefore are not influenced by, the multiple-choice section of the examination, which is scored separately by machine. Student scores on both parts of the examination are combined and used by the chief faculty consultant to determine the levels of student performance on the AP 1 to 5 grading scale.

The Reading

In June the faculty consultants meet for six days on a college campus to score the free-response sections of the AP Chemistry Examination. The chief faculty consultant divides the faculty consultants into groups, each under the direction of a designated faculty consultant called a table leader. One or more table leaders with their group of faculty consultants is assigned to score each free-response question, depending on the number of students who chose to answer it. The table leaders train their groups to score their designated question, and scoring of student papers commences according to standards developed as described below. Each answer booklet is circulated among the various groups until all the student responses in that booklet have been scored. The finished booklets are then removed from the Reading site and the scores are entered into computers and matched with the students' multiple-choice section scores. Composite scores are calculated and these and other data are provided to the chief faculty consultant for the grade-setting session, which occurs shortly after the Reading is over.

Developing Free-Response Scoring Standards

Scoring standards for the free-response questions are a consideration throughout the development of the examination. Members of the AP Chemistry Development Committee submit suggested scoring standards with each question that they write. Scoring standards are discussed further when questions are revised and chosen by the committee to be included in an examination. At this stage, consideration is given to potential difficulties that might interfere with the reliable scoring of a question, and the scoring standard may be revised accordingly. Prior to the Reading, the chief faculty consultant generates a draft of the scoring standard for each of the nine questions in the free-response section, taking into consideration issues raised during previous reviews. The general scoring guide for the free-response questions is as follows:

Problems	9 points each
Chemical Reactions	3 points each (15 points total)
Essays	8 points each

Two days before the Reading begins, the chief faculty consultant meets with the table leaders to review the draft standards, and the group reaches a consensus on a possible standard for each question. The table leaders break into groups to test the standards against a number of student responses. During this phase of the process, the standards may be modified somewhat. Meeting again as a whole group, the chief faculty consultant and the table leaders reach another consensus on the standards, after which each table leader is assigned to a particular question and is also assigned a list of faculty consultants with whom he or she will score the question during the Reading.

On the first day of the Reading, the table leaders train the faculty consultants in applying the scoring standards to a set of sample student responses selected for that purpose. During this process, the standards are refined and may be modified slightly once again. After the group is proficient in applying the scoring standards, the actual scoring of the student papers begins. The final results of the rigorous standard-setting procedure described above are standards that can be applied reliably not only to the common methods of solution seen in the student responses, but also to common errors and to alternative or unusual approaches.

Because various student responses to a given question are scored over a six-day period by more than one faculty consultant, it is important to monitor the application of the standards during the Reading. This is done by having a certain number of student papers independently graded more than once, either by different faculty consultants, or by the same consultant at

a later time. The original scores are concealed from subsequent faculty consultants, and the two sets of scores are then compared. The checking of one consultant against another quickly identifies any remaining ambiguities that may exist in the standards and allows their further refinement, to help assure that a student's score is independent of the person scoring the paper. Checking a consultant against his or her own work also helps assure that a student's score is independent of what day or time the paper is scored. Rarely is there a discrepancy of more than 1 point on the scale. Other procedures help maintain consistent scoring standards. After the Reading is underway, the table leaders select and score another series of questions for yet another kind of consistency check. This one does not compare the faculty consultants with themselves, but rather it compares them with the other faculty consultants in their group and individually with the table leaders.

The philosophy of the faculty consultants in scoring the free-response questions is to award credit for correct work. When questions involve calculations, most of the points awarded are given for setting up the solution correctly rather than actually carrying out the computation. Partial credit is awarded within each part of a question, so students should be encouraged to show their work. Faculty consultants try to determine whether an incorrect answer to a previous part has been correctly used in a subsequent part of a question. Full credit for the latter part may be awarded if the consultant can successfully trace the student's work to make that determination. Students should also be encouraged to continue on to later parts of a question if they get stuck at some point. Parts of a question are often independent of each other; even when they are dependent, credit can be earned on later parts when earlier answers are missing. Also, a student's explanation of what he or she would do, if possible, could earn some credit. Finally, when final answers are numerical, students should pay attention to significant figures since 1 point is deducted (once per problem) if the number of significant figures in a student's answer differs by more than one from the appropriate number.

■ FREE-RESPONSE QUESTIONS, SCORING GUIDES, AND SAMPLE STUDENT ANSWERS

On the pages that follow are a selection of student responses to each of the questions that made up the free-response section of the 1994 Advanced Placement Examination in Chemistry. Also included are the standards that were applied in the scoring process, and an explanation of why each response received the score it did. For each question, two student responses have been selected to illustrate a superior answer and one of somewhat lower quality.

From our experience in reading Advanced Placement Examinations we know that no set of scoring standards can possibly anticipate the creativity of high school students in developing solutions to problems. Therefore, you should understand that readers make every possible effort to give credit for every response that reflects an understanding of basic principles of chemistry regardless of how far the approach used deviates from what might be a more conventional route developed in the standards.

In developing the standards for the 1994 AP Chemistry Exam, the chief faculty consultant had the assistance of 11 faculty consultants who served as table leaders, and two test development specialists from ETS. The group met for two days prior to the Reading. After a draft set of standards was established, the application of the standard for each question was tested with about 100 papers. The standards were then reviewed in the light of that experience and either revised accordingly or adopted.

If a student made an error in part (a) of a four-part problem and the answer to part (a) was essential to working the rest of the problem, the reader of the paper was obliged to work through the solutions to the subsequent parts of the question with the erroneous answer to *part a.* Thus, every effort was made to reward the students with points for the appropriate application of chemical principles. Students were, however, penalized for mathematical errors and errors in significant figures (exceeding one too many or one too few) to the maximum extent of 1 point for an error of each kind on any one problem.

Question 1

This required problem provided students with an opportunity to demonstrate their understanding of an ionic equilibrium and the common ion effect, to make a prediction based on their calculations, and to relate solubility data to thermodynamics.

Scoring Standards

(a) $K_{sp} = [Mg^{2+}][F^-]^2$ *(1 pt.)*

$= (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2$

$= 7.09 \times 10^{-9}$ *(1 pt.)*

Note: if number of significant figures in final answer differs by more than one from the appropriate number, 1 point is deducted ONCE PER PROBLEM.

(b) $K_{sp} = [Mg^{2+}](2x + 0.100)^2$ $\quad 2x \ll 0.100$ *(1 pt.) for proper substitution*

$7.09 \times 10^{-9} = [Mg^{2+}](0.010)^2$

$[Mg^{2+}] = (7.09 \times 10^{-9})/(10^{-2})$

$= 7.09 \times 10^{-7}\ M$ *(1 pt.)*

Note: *OK* if 0.102 is used for $[F^-]$, then $K_{sp} = 6.76 \times 10^{-7}$

(c) $[Mg^{2+}]$: $100.0 \times 3.00 \times 10^{-3} = 300.0 \times [Mg^{2+}]$

$[Mg^{2+}] = 1.00 \times 10^{-3}\ M$

$[F^-]$: $200.0 \times 2.00 \times 10^{-3} = 300.0 \times [F^-]$

$[F^-] = 1.33 \times 10^{-3}\ M$

(1 pt.) if <u>both</u> concentrations are correct

Q = Ion Product $= [Mg^{2+}][F^-]^2$

$= (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2$ **

$= 1.77 \times 10^{-9}$ *(1 pt.)*

Since $Q < K_{sp}$, no precipitate will form *(1 pt.)*

Note: conclusion must be consistent with Q value.

** Correct substitution and calculation of the *wrong* concentration values earns the second point, but not the first.

(d) Solubility of MgF_2 decreases with increasing temperature, thus dissolution process is <u>exothermic</u> *(1 pt.)*

$$MgF_2(s) \rightleftharpoons Mg^{2+} + 2\ F^- + Q \text{ (or } H)$$

Reason:

EITHER

i) Increased temperature puts a stress on the system (Le Châtelier). The system will reduce the stress by shifting the equilibrium in the endothermic (left) direction

OR,

ii) a data supported argument such as comparing ion concentrations, calculating second K_{sp} and giving proper interpretations.

(1 pt.)

Sample Student Response 1

a) $K_{sp} = [Mg^{2+}][F^-]^2$

$1.21 \times 10^{-3}\ M \cdot 1.21 \times 10^{-3}\ \frac{mol\ Mg^{2+}}{L} \times \frac{2\ mol\ F^-}{1\ mol\ Mg^{2+}} = 2.42 \times 10^{-3}\ M\ F^-$

$K_{sp} = [1.21 \times 10^{-3}\ M][2.42 \times 10^{-3}\ M]^2 = \boxed{7.09 \times 10^{-9}}$

b) $K_{sp} = [Mg^{2+}][F^-]^2 \Rightarrow [Mg^{2+}] = \frac{K_{sp}}{[F^-]^2} = \frac{(7.09 \times 10^{-9})}{(0.100)^2} = \boxed{7.09 \times 10^{-7}\ M\ Mg^{2+}}$

c) Mg^{2+}: $3.00 \times 10^{-3}\ \frac{mol}{L} \times (0.100\ L) = 0.0003\ mol\ Mg^{2+} \times \left(\frac{1}{0.300\ L}\right) = 0.001\ M\ Mg^{2+}$

F^-: $2.00 \times 10^{-3}\ \frac{mol}{L} \times (0.200\ L) = 0.0004\ mol\ F^- \times \left(\frac{1}{0.300\ L}\right) = 0.00133\ M\ F^-$

$Q = [Mg^{2+}][F^-]^2 = (0.001)(0.00133)^2 = 1.78 \times 10^{-9}$

$Q < K_{sp}$, ∴ a precipitate will not form

d) As the temperature increases, the concentration of Mg^{2+} ions decreases. By LeChatlier's principle, if $[Mg^{2+}]$ decreases, the reaction favors the reactants:

$MgF_2 \longleftarrow Mg^{2+} + 2F^-$

Because the addition of heat caused this change, the heat must be on the products side of the equation in order to shift the reaction towards the reactants:

$MgF_2 \longleftarrow Mg^{2+} + 2F^- + heat$

When heat is a product on a reaction, that reaction is exothermic (heat is released).

Comment: This paper earned all of the 9 possible points. Although the student did not explicitly indicate that the simplifying approximation was being made in **part b**, it clearly was; and the substitution and calculation were made correctly. The calculations in **part c** were clear and correct and the conclusion based on the relationship between Q_c and K_{eq} was unambiguous. The analysis and conclusion in **part d** were straightforward and to the point.

Sample Student Response 2

① (a) $K_{sp} = [Mg^{2+}][F^-]^2$

at 18°C: $[Mg^{2+}] = 1.21 \times 10^{-3}\ M$

$[F^-] = 2[Mg^{2+}] = 2(1.21 \times 10^{-3}\ M) = 2.42 \times 10^{-3}\ M$

$K_{sp} = (1.21 \times 10^{-3}\ M)(2.42 \times 10^{-3}\ M) = 2.93 \times 10^{-6}$

(b) $KF(s) \longrightarrow K^+(aq) + F^-(aq)$

0.100 mole 0.100 mole

$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$

$x \qquad 2x$

$K_{sp} = [Mg^{2+}][F^-]^2$

$2.93 \times 10^{-6} = x(2x + 0.100)^2$

Assume $x << 0.100$

$2.93 \times 10^{-6} = 0.0100x$

$x = 2.93 \times 10^{-4} = [Mg^{2+}]$

(c) $Mg(NO_3)_2 \longrightarrow Mg^{2+} + 2NO_3^-$

? moles $Mg^{2+} = 100\text{ml} \times \frac{3.00 \times 10^{-3}\text{ moles}}{1000\text{ ml}} = 3.00 \times 10^{-4}$ moles

$NaF \longrightarrow Na^+ + F^-$

? moles $F^- = 200\text{ ml} \times \frac{2.00 \times 10^{-3}\text{ moles}}{1000\text{ ml}} = 4.00 \times 10^{-4}$ moles

$[Mg^{2+}] = \frac{3.00 \times 10^{-4}\text{ moles}}{.300\text{ L}} = 1.00 \times 10^{-3}\ M$

$[F^-] = \frac{4.00 \times 10^{-4}\text{ moles}}{.300\text{ L}} = 1.33 \times 10^{-3}\ M$

$[Mg^{2+}][F^-]^2 = (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.33 \times 10^{-9} < K_{sp} = 2.93 \times 10^{-6}$

No ppt will form

(d) at 18°C, $[Mg^{2+}] = 1.21 \times 10^{-3}\ M$

at 27°C, $[Mg^{2+}] = 1.17 \times 10^{-3}\ M$

$[Mg^{2+}]$ decreased with the rise in temperature. The added energy was not used to dissolve ~~additional~~ $MgF_2(s)$ in H_2O. The dissolving of MgF_2 is exothermic

Comment: In **part a** of this question, the student lost a point for failing to square the concentration of the fluoride ion in the calculation. This was a common flaw in **part a**. Although the student had an incorrect value for K_{eq} in **part a**, he or she earned full credit in **part b** for using it correctly in the calculations. The student lost a point in **part c** for the mathematics error made in calculating Q_c. Although the analysis in **part d** is somewhat unusual, it is clear the student understands the implications of raising the temperature on a system in equilibrium in which the forward reaction is exothermic, thus full credit was awarded for this part. The total score for this paper was 7.

Question 2

Students frequently did **parts a** and **b** correctly (although many omitted units in **part b**). Credit was given in (**ii**) of **part a** if the rate law given was consistent with the kinetic orders of (i). The fact that the initial concentrations of the reactants in **part c** were not equal led many students to miss this part. Many students who lost points in **part c** simply failed to take advantage of the simple stoichiometry but tried to plug concentrations into the rate law. **Part d** was difficult for many students who tried to show that the reaction stoichiometry was consistent with the rate-determining step. Many students who correctly chose Step II of the mechanism as the rate-determining step simply stated that because $2NO \rightleftharpoons N_2O_2$, then $[N_2O_2] = [NO]^2$ and lost a point as a result.

Scoring Standards

(a) (i) From exps. 1 and 2: Doubling $[H_2]$ while keeping [NO] constant doubles the rate, therefore the reaction is *first order* in $[H_2]$. (*1 pt.*) *for order and justification*

From exps. 3 and 4: Doubling [NO] while keeping $[H_2]$ constant quadruples the rate, therefore the reaction is *second order* in [NO]. (*1 pt.*) *for order and justification*

(ii) $Rate = k[H_2][NO]^2$ (*1 pt.*)

Note: full credit earned for (ii) as long as rate expression is consistent with orders in (i).

(b) $k = \dfrac{Rate}{[H_2][NO]^2}$

From exp. 1: $k = \dfrac{1.8 \times 10^{-4}\ M/\text{min}}{(1.0 \times 10^{-3}\ M)(6.0 \times 10^{-3}\ M)^2}$ (*1 pt.*) *for value*

$= 5.0 \times 10^{3}\ M^{-2}\ \text{min}^{-1}$ (*1 pt.*) *for units*

Note: same result from initial rate data from all 4 experiments.

(c) Stoichiometry: $NO:H_2$ is 1:1

When 0.0010 mole of H_2 had reacted, it must have reacted with 0.0010 mole of NO; thus

$[NO]$ remaining $= 0.0060 - 0.0010 = 0.0050\ M$. (*1 pt.*)

(d) (i) For I: $K_{eq} = \dfrac{[N_2O_2]}{[NO]^2}$

For II: $Rate = k[H_2][N_2O_2]$

$[N_2O_2] = K_{eq}[NO]^2$

$Rate = k'[H_2][NO]^2$ *(1 pt.)*

Note: there must be some clear algebraic manipulation showing that $[N_2O_2]$ is <u>proportional</u> (NOT equal) to $[NO]^2$.

<u>Step II</u> is the rate-determining step. *(1 pt.)*

(ii)

I:	NO	+	NO			N_2O_2		
II:	N_2O_2	+	H_2	$\longrightarrow$	H_2O	+	N_2O	
III:	N_2O	+	H_2	$\longrightarrow$	N_2	+	H_2O	*(1 pt.)*
I + II + III:	2 NO	+	2 H_2	$\longrightarrow$	N_2	+	2 H_2O	

Sample Student Response 1

a) i) comparison of 1 and 2 → constant [NO], double $[H_2]$, double rate
∴ reaction is first order in H_2

comparison of 3 and 4 → double [NO], constant $[H_2]$, quadruple rate
∴ reaction is second order in NO

ii) rate = $k[H_2][NO]^2$

b) rate = $k[NO]^2[H_2]$

$k = \frac{rate}{[NO]^2[H_2]}$ → I will use data for experiment 1

$k = \frac{1.8\times10^{-4}\ M/min}{(6.0\times10^{-3}\ M)^2(1.0\times10^{-3}\ M)}$

$k = 5.0\times10^{3}\ M^{-2}\ min^{-1}$

c) $2\,NO_{(g)} + 2\,H_{2(g)} \rightarrow N_{2(g)} + 2\,H_2O_{(g)}$

	[NO]	$[H_2]$	
start	.0060 M	.0020 M	
change	−.0010 M	−.0010 M	(1:1 ratio between NO and H_2)
end	.0050 M	.0010 M	

$[NO] = 5.0\times10^{-3}\ M$ when half of H_2 is consumed in experiment 2

d) the rate-determing step is the second step: $N_2O_2 + H_2 \xrightarrow{\text{slow}} H_2O + N_2O$

i) rate = $k_2[N_2O_2][H_2]$ → N_2O_2 is an intermediary, so I will substitute for it

$NO + NO \rightleftarrows N_2O_2$

$K_{eq} = \frac{[N_2O_2]}{[NO][NO]}$

$[N_2O_2] = K_{eq}[NO]^2$

rate = $k[NO]^2[H_2]$ → this agrees with part a)

ii) $NO + NO \rightleftarrows N_2O_2$ (fast equilibrium)

$N_2O_2 + H_2 \rightarrow H_2O + N_2O$ (slow)

$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

$2NO + N_2O_2 + 2H_2 + N_2O \rightarrow N_2O_2 + 2H_2O + N_2 + N_2O$

$2NO + 2H_2 \rightarrow 2H_2O + N_2$ → this equals the overall reaction

Comment: In **part a**, the kinetic orders derived are well justified and the rate law is consistent with them. In **part b**, the student derives an expression for the rate constant from the rate law and even specifies the number of the experiment from which he or she takes the experimental data in evaluating *k*. In **part c**, the student systematically tabulates the concentrations of the reactants in a fashion similar to that used in equilibrium problems and clearly recognizes the stoichiometric ratio of hydrogen to nitric oxide. The student earns all 3 of the possible points in **part d** by choosing the second step of the mechanism as the rate-determining step, showing that its rate is consistent with the rate law, and demonstrating that the sum of the three steps in the mechanism is equal to the overall reaction stoichiometry. This was an excellent answer that received a perfect score of 9.

Sample Student Response 2

a)(i) The order for NO is 2; this can be inferred from the data in experiments 3 and 4. As the [NO] is doubled, the rate of formation is quadrupled. Thus the rate is dependant on the square of [NO]
The order for H_2 is 1, this can be inferred from the data in experiments 1 and 2. As the $[H_2]$ is doubled, the rate is also doubled. Thus the rate is dependent on the $[H_2]$ itself.

(ii) $r \propto k[NO]^2[H_2]$

b) $r = k[NO]^2[H_2]$

$1.8\times10^{-4}\,M/min = k(.0060\,M)^2(.0010\,M)$

$1.8\times10^{-4}\,M/min = k(3.6\times10^{-8}\,M^3)$

$k = 5.0\times10^3\,min^{-1}M^{-2}$

c) $r \propto k[NO]^2[H_2]$

Experiment 2 -

$3.6\times10^{-4} = 5.0\times10^3\,[NO]^2[H_2]$

$3.6\times10^{-4} = 5.0\times10^3\,[X^2][.0010]$

$3.6\times10^{-4} = 5.0\,X^2$

$X = 8.5\times10^{-3}\,M = [NO]$

d) The rate determining step in this sequence of elementary step is Step II. ($N_2O_2 + H_2 \rightarrow H_2O + N_2O$). If the rate determining step is II, then $r \propto [N_2O_2][H_2]$. Since the $[N_2O_2] \propto [NO]^2$ from Step I, then the overall rate $\propto [NO]^2[H_2]$. This is consistent with the observed rate law: $r \propto [NO]^2[H_2]$
This step is also consistent with the overall stoichiometry of the rxn. because when the

Comment: Although the student expresses the rate law in **part (ii)** of **a** as a proportionality, the equation is written correctly in **part b** and full credit is given in **part a**. The solution to **part b** is clear and straightforward. The student runs into trouble in **part c** by substituting concentrations into the rate expression (a common error) and failing to note the 1:1 stoichiometry in the reaction. In **part d**, a point was deducted because the student did not show that the mechanism was consistent with the reaction stoichiometry. The total score for this answer was 7.

Question 3

Although the difficulty of this question was judged by the readers to be similar to that of question 2, significantly less than half of the examinees chose to work on this problem. Points were frequently lost in **part a** when students failed to consider the water vapor in the collected gas. Failure to read **part b** carefully led many students to calculate the number of molecules of hydrogen rather than water vapor. In **part c** credit was awarded for answers derived from equating the average kinetic energies of the gas molecules or by calculating the root-mean-square speeds of the molecules of the two gases. In **part d** many students cited the difference in the masses of the two molecules and lost credit for the explanation part of the question.

Scoring Standards

(a) $n = \frac{PV}{RT} = \frac{(721)(0.090)}{(62.4)(298)} = 3.49 \times 10^{-3}$ mol H_2

25°C $\longrightarrow$ 298 K (*1 pt.*)

745 - 24 = 721 mm Hg (*1 pt.*)

calculation of moles of H_2 (*1 pt.*)

(b) $\frac{(23.8)(0.090)}{(62.4)(298)} = 1.15 \times 10^{-4}$ mol H_2O (*1 pt.*)

$(1.15 \times 10^{-4})(6.03 \times 10^{23}) = 6.92 \times 10^{19}$ molecules H_2O (*1 pt.*)

(c) The average kinetic energies are equal, so

$$(\tfrac{1}{2}mv^2)_{H_2O} = (\tfrac{1}{2}mv^2)_{H_2} .$$

$$\frac{v_{H_2}}{v_{H_2O}} = \sqrt{\frac{MM_{H_2O}}{MM_{H_2}}} = \sqrt{\frac{18}{2}} = 3$$

(*1 pt.*) *for formula*
(*1 pt.*) *for calculation*

Note: credit also given for correct use of $v_{rms} = \sqrt{\frac{3RT}{M}}$.

(d) H_2O deviates more from ideal behavior. (*1 pt.*)

Explanation:

EITHER

i) The volume of the H_2O molecule is larger than that of the H_2 molecule

OR,

ii) The intermolecular forces among H_2O molecules are stronger than those among H_2 molecules

} (*1 pt.*)

Sample Student Response 1

(a) $P_{H_2} = P_{tot} - P_{H_2O} = 745\ mm\ Hg - 23.4\ mm\ Hg = 721\ mm\ Hg$ $\quad PV=nRT$

$V = 10.0\ mL \left(\frac{1\ L}{1000\ mL}\right) = 9.00 \times 10^{-2}\ L$ $\quad T = 25°C + 273 = 298\ K$

$n = ?$ $\quad R = 62.4\ L \cdot mm\ Hg / mole \cdot K$

$(721\ mm\ Hg)(9.00 \times 10^{-2}\ L) = (n)(62.4\ L \cdot mm\ Hg)(298\ K)$

$n = 3.49 \times 10^{-3}$ moles H_2 gas

(b) $PV=nRT$ $\quad P_{H_2} = 23.8\ mm\ Hg$ $\quad V = 9.00 \times 10^{-2}\ L$ $\quad R = 62.4\ L \cdot mm\ Hg/mole \cdot K$ $\quad T = 298\ K$ $\quad n = ?$

$(23.8\ mm\ Hg)(9.00 \times 10^{-2}\ L) = n(62.4\ L \cdot mm\ Hg)(298\ K)$

$n = 1.15 \times 10^{-4}$ moles H_2O $\quad$ molecules $H_2O = 1.15 \times 10^{-4}\ mole\ H_2O \left(\frac{6.02 \times 10^{23}}{1\ mole}\right) = 6.93 \times 10^{19}$ molecules H_2O

(c) $KE = \frac{1}{2}mv^2$ $\quad \frac{1}{2} m_{H_2O} (v_{H_2O})^2 = \frac{1}{2} m_{H_2} (v_{H_2})^2$

$KE_{H_2O} = KE_{H_2}$

$\left(\frac{v_{H_2}}{v_{H_2O}}\right)^2 = \frac{m_{H_2O}}{m_{H_2}}$ $\quad \frac{v_{H_2}}{v_{H_2O}} = \sqrt{\frac{m_{H_2O}}{m_{H_2}}}$

$m_{H_2O} = MM = (1.007\ g)2 + (16.00) = 18.02\ g/mole$

$m_{H_2} = MM = (1.007\ g)2 = 2.0154\ g$

$\frac{v_{H_2}}{v_{H_2O}} = \sqrt{\frac{18.02\ g}{2.0154\ g}} = \sqrt{8.94} = 2.99$ $\quad \frac{v_{H_2}}{v_{H_2O}} = 2.99$

(d) H_2O deviates more from ideal behavior. This can be noticed by the fact that the ratio of average speeds of H_2 to H_2O is about 3. This should also mean that on the sample that is collected the partial pressure of H_2O should be 1/3 the partial pressure of the H_2 collected. This can be explained by the intermolecular force of hydrogen bonding in the H_2O. The H_2O molecules are held closer together by Hydrogen bonds so are harder to separate and change to gasses form. H_2O has a lower vapor pressure than it should and deviates from ideal the greatest because ideal gases have no intermolecular forces.

Comment: In **part a**, the conversion of Celsius temperature to Kelvins, the application of Dalton's Law, and the use of the ideal gas equation were all done correctly. In **part b**, the student clearly recognized the relationship between the pressure of a gas and the number of moles present and made the correct calculation using N_A. The solution to **part c** is clear and straightforward. The analysis in **part d** wanders somewhat, but credit was awarded because the student was aware that the hydrogen bonding in water is an intermolecular force and that ideal gases experience no intermolecular forces. This response received a score of 9 points.

Sample Student Response 2

a) $PV=nRT$ $P=\frac{745-23.8}{760}=.949$ atm

$V=.09L$

$n=X$

$R=.0821$

$T=273+25=298°K$

$(.949)(.09)=X(.0821)(298)$

$X=\frac{(.949)(.09)}{(.0821)(298}$ $X=.00349$ moles H_2

b) $P=\frac{238}{760}$ $V=.09$ $n=X$ $R=.0821$ $T=298°K$

$PV=nRT$

$(.0313)(.09)=X(.082)(298)$

$X=\frac{(.0313)(.09}{(.0821)(298}$

$X=.000115\ (6.022\times10^{23})=6.934\times10^{19}$ molecules

c) $\frac{9\text{ gm } H_2O}{118/2}$ / $\frac{\text{gm } H_2}{19}$

d) H_2O deviates more than H_2, because H_2O has a higher molar mass than H_2, which makes its collisions with other gas molecules and its container more inelastic the that of H_2

Comment: The correct answers were obtained in both **parts a** and **b** in routine fashion. Although the answer in **part b** was expressed in too many significant figures, no points were deducted because the number of significant figures given exceeded the appropriate number by only one. The student earned no credit in **part c** since the response reflected no recognition of the relationship between molecular speed and the square root of the molecular mass nor the inverse relationship between molecular mass and speed. In **part d**, the student correctly identifies water as the gas that deviates more from ideal behavior, but, like many students, attributed that greater deviation to water's larger molar mass. The total score was 6 points.

Question 4

The ability to write the formulas of chemical species from their names and knowing the reactions that commonly encountered chemical systems undergo apparently continues to confound AP Chemistry students. Historically, the performance of students on the required "equation" question has reflected their lack of exposure to enough descriptive chemistry. The performances of students on this year's required equation question, however, were significantly improved over 1993 *(mean scores of 5.3 versus 4.4). Only 0.7% of the students taking the examination had perfect scores of 15 on this question.*

Scoring Standards

Guiding principles:

1) Each reaction is worth a total of 3 points
2) Reactants +1 point; products +2 points
3) Ignore balancing and states
4) Inappropriate ionization - maximum 1 point penalty per equation

(a) $CN^- + Ag^+ \longrightarrow Ag(CN)_2^-$

Note: any complex ion of Ag with cyanide with consistent charge earns 3 points; AgCN given as product earns 1 product point

(b) $Mn^{2+} + S^{2-} \longrightarrow MnS$

Note: If Mg used instead of Mn, maximum possible score is 2 points

(c) P_4O_{10} (or P_2O_5) + $H_2O \longrightarrow H_3PO_4$

Note: Acidic species (H^+ or oxyacid of phosphorus) earns 1 product point;
P in +5 oxidation state in oxyanion earns 1 product point;
anions of oxyacids of phosphorus require H^+ for full credit for products

(d) $(NH_4)_2CO_3 \longrightarrow NH_3 + H_2O + CO_2$

Note: Any one product earns 1 point; all three earns 2 product points
$NH_4OH + CO_2$ earns 1 product point
$NH_3 + H_2CO_3$ earns 1 product point

(e) $CO_2 + OH^- \longrightarrow HCO_3^-$

Note: $CO_3^{2-} + H_2O$ as products earns 2 product points
CO_3^{2-} alone as product earns 1 product point
$HCO_3^- + H_2O$ earns 1 product point

(f) $H^+ + Cl^- + KMnO_4 \longrightarrow K^+ + Mn^{2+} + Cl_2 + H_2O$

Note: HCl and MnO_4^- acceptable as reactants
Any valid redox product earns 1 point
All four products earns 2 points
K^+ and/or H_2O only as products earns no credit
If both H^+ and H_2O omitted, then maximum of 2 points possible

(g) $Na + H_2O \longrightarrow H_2O + Na^+ + OH^-$

Note: All three products earns 2 product points
Any vaid redox product earns 1 product point

(h) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

Note: All three products earns 2 product points
Any valid redox product earns 1 product point
H_2O only earns no credit
If $Cl^- \longrightarrow Cl_2$ instead of $Fe^{2+} \longrightarrow Fe^{3+}$, then maximum of 2 points possible

Sample Student Response 1

B.) $Mn^{2+} + S^{2-} \rightarrow MnS$

D.) $(NH_4)_2CO_3 + heat \rightarrow NH_3 + H_2O + CO_2$

F.) $H^+ + Cl^- + KMnO_4 \rightarrow Cl_2 + Mn^{2+} + K^+ + H_2O$

G.) $Na + H_2O \rightarrow Na^+ + OH^- + H_2$

H.) $Cr_2O_7^{2-} + Fe^{2+} \xrightarrow{H^+} Cr^{3+} + Fe^{3+}$

Comment: This response failed to earn a perfect score for omitting the water in **equation h**. This was a common error in the redox reactions. The total score for this answer was 14 points.

Sample Student Response 2

(g) $Na + H_2O \rightarrow NaOH + H_2$

(a) $CN^- + Ag^+ \rightarrow AgCN$

(b) $Mn^{2+} + S^{2-} \rightarrow MnS$

(d) $(NH_4)_2CO_3 \xrightarrow{heat} NH_3 + CO_2 + OH^-$

(e) $CO_2 + OH^- \rightarrow CO_3^- + H_2O$

Comment: A point was lost in **equation g** for failure to represent sodium hydroxide as an ionized species. In **equation a**, a point was deducted for the failure to recognize that a complex ion was formed (see the Scoring Standards). In **equation d**, a "product" point was deducted for the hydroxide ion (rather than water). In **equation e**, the student lost a point for the incorrect charge on the carbonate ion product. The score for this response was 11 points.

Question 5

For this required essay question involving simulated laboratory exercises, students were asked to explain the result of a change in conditions on an illustrated experimental situation. The committee hoped it would encourage a significant increase in the laboratory component in AP Chemistry courses.

Scoring Standards

(a) Volume decreases in beaker A; the concentration decreases in beaker B (either observation earns 1 point provided other one is not wrong) *(1 pt.)*

The vapor pressure of pure H_2O is greater than the vapor pressure of H_2O in solution,

OR,

the rate of evaporation of H_2O molecules from pure H_2O is greater than that from the sugar solution, while the condensation rates are the same. *(1 pt.)*

(b) The water will begin to boil (or evaporate). *(1 pt.)*

The external pressure on the water will become equal to the vapor pressure of the water, causing it to boil,

OR,

the drop in external pressure causes the boiling point to drop to the temperature of the water. *(1 pt.)*

(c) Solid copper is deposited on the zinc strip; the zinc strip goes into solution. No reaction occurs with silver. *(1 pt.)*

Zinc is a better reducing agent or a more active metal than copper and will be oxidized. Silver is a less reactive metal than copper is. *(1 pt.)*

(d) Two layers will form, one of which is colored. *(1 pt.)*

Iodine is nonpolar and will dissolve in TTE.
Water is polar and will not dissolve in TTE. *(1 pt.)*

Note: placement of I_2 must be correctly indicated for 2nd point.

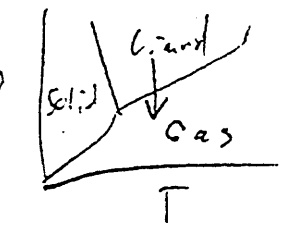
Sample Student Response 1

a. The pure water in Beaker A evaporates and condenses in beaker B, lowering the concentration of the sugar solution by increasing the volume of solvent. The system is seeking equilibrium at maximum entropy. Both solutions should have a concentration of 5% sugar to be equal. And because the sugar molecules don't evaporate and they lower the ability of the water in beaker B to evaporate, more water evaporates from A than B and that which condenses in B tends to stay there longer than it would in A.

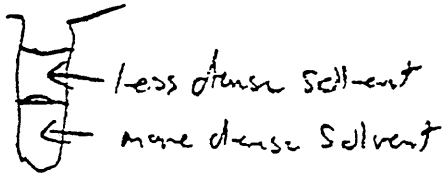
b. The water will boil. See diagram below. It boils because the vapor pressure drops below that needed to sustain gas at that temperature. So the water evaporates until the vapor builds enough pressure to sustain equilibrium between liquid and gas, and this doesn't happen because the vapor is constantly being removed by the vaccum pump. So the water continues to boil away.

c. Nothing happens to the Silver. The Zinc displaces the Copper from its solution and copper crystals on the Zinc surface. This happens due to the activity of the metals. Metals with greater activities displace those with lesser activities from their solutions. The activity order for the three metals involved is Zn > Cu > Ag.

6.



d.



d. I_2 is non polar, H_2O is. Polar solvents tend to dissolve polar solutes and vice versa. Like dissolves like. The Iodine will leave the water in favor of the non polar TTE solvent. H_2O is polar and TTE is not, so neither will dissolve in the other. The system will appear with the less dense of the solvents sitting on top of the more dense solvent with the I_2 dissolved in TTE.
* due to buoyancy -

Comment: The response in **part a** presents an unusual combination of a reference to an increase in entropy and the differential rates of evaporation of pure water and an aqueous solution of sugar. In **part b**, the response does not match the standards but clearly indicates that the student understands what is required for this system to reach equilibrium and why this one never can. The student's response to **part c** essentially embodies the ideas in the standards. The response to **part d** quite simply covers all of the bases. One would have to look hard for a place to deduct points from this response, which received the maximum score of 8 points.

Sample Student Response 2

a) The amount of pure H_2O should decrease, and the concentration of sugar solution should decrease. A system will try to equilize the concentrations within it, and so the H_2O goes to the sugar solution to decrease its concentration.

b) The water will boil, for boiling point is in direct proportion with pressure, all other factors being equal; lowering pressure allows the H_2O to boil at room temp.

c) Zinc, being a good reducing agent, will reduce the Cu^{+2} to Cu; thus, copper metal will form on the zinc strip. Silver, however is a much poorer reducing agent (Ag^+ is below Cu^{+2} on the chart) and thus will not reduce the copper; we will find no change on the silver strip.

Zn^{+2} (is above Cu^{+2} on the reduction potential)

d) The I_2 solution will not mix with the TTE, but rather the two will remain as separate layers in the test tube. The nonpolar TTE solvent cannot dissolve the polar water-I_2 solution.

Comment: This paper earned a score of 6. The response in **part a** was seen in many papers. The awarding of the "observation point" was routine, but simply stating that there is a tendency for the concentrations of the two systems to become equal was insufficient to earn the "explanation point." Both the "observation" point and the "explanation" point were clearly articulated in the response to **part b**. The student's response in **part c** also clearly earns credit for both the "observation" and "explanation" points. In **part d** a point was lost since there was a clear statement that the solutions would separate and two layers would form. Failure to specify that the iodine will be in the TTE cost this student a point.

Question 6

The importance of thermodynamics in even an introductory chemistry course is reflected by the fact that it is almost a standard essay topic on the AP Chemistry Examination. In **part a** of this question, students were given the opportunity to relate the entropy change for a reaction to the stoichiometry and to the phase change that takes place as reactants are converted to products. **Parts b** and **c** gave the student an opportunity to demonstrate an understanding of the implications of a change in the temperature on the spontaneity of a reaction and the K_{eq} of a system at equilibrium. In each of the **parts a, b,** and **c,** the writing of an equation alone was not sufficient to earn the "explanation" point; the student was required to connect the equation to the issue to be explained. In **part d,** a knowledge of the Gibbs-Helmholtz equation and the dependence of the enthalpy and entropy changes on temperature were required. Points were not deducted for sloppiness or confusion relative to the differences between the standard and nonstandard values of changes in free energy, entropy, or enthalpy.

Scoring Standards

(a) Statement that ΔS^0 is negative *(1 pt.)*

3 moles of gas ⟶ 2 moles of gas plus solid,
(3 moles ⟶ 2 moles earns no points)
OR,

2 gases ⟶ 1 gas + solid, *(1 pt.)*

OR,

use of $\Delta G^0 = \Delta H^0 - T\Delta S^0$ with $\Delta G^0 \longrightarrow 0$

Note: If statement is that ΔS^0 is positive, then explanation of
3 moles gas ⟶ 5 moles of gas earns 1 point
(3 moles ⟶ 5 moles earns no points)
If correct explanation for ΔS^0 being negative is given but wrong sign is stated, 1 point is earned.

(b) ΔG^0 is less negative, goes to 0, goes +, gets larger *(1 pt.)*

Explanation using $\Delta G^0 = \Delta H^0 - T\Delta S^0$ *(1 pt.)*

Note: if answer to (a) is that ΔS^0 is positive, then full credit can be earned here for correct reasoning based on that assumption. An explanation that uses Le Châtelier's principle based on sign of ΔH^0 is NOT valid here since system not at equilibrium.

(c) K_{eq} decreases (exponent ⟶ more negative) as T increases

OR, *(1 pt.)*

K_{eq} goes from > 1, to 1, to < 1, as T increases

Correct explanation using the equation
$\Delta G^0 = -RT \ln K_{eq}$ (or $\ln(K_1/K_2) = \Delta H^0/R(1/T_2 - 1/T_1)$

OR, *(1 pt.)*

higher T favors the reverse reaction (Le Châtelier)
because the forward reaction is exothermic

Note: if answer for (a) is that ΔS^0 is positive then statement that K_{eq} will decrease or increase depending on the relative magnitude of T and ΔG^0 change earns 2 points. Recognition that BOTH ΔG^0 and T are changing in $\Delta G^0 = -RT \ln K_{eq}$ is necessary. Or, ignoring part (a), use of $\Delta H^0 < 0$ explanation to correctly predict that K_{eq} will decrease earns 2 points.

(d) Since $\Delta G^0 = 0$ at this point, the equation is $T = \Delta H^0/\Delta S^0$. *(1 pt.)*
($\Delta G^0 = \Delta H^0 - T\Delta S^0$ is NOT sufficient without $\Delta G^0 = 0$.)

Prediction is not exact because ΔH^0 and/or ΔS^0 vary with T *(1 pt.)*

General Note: For parts (a), (b), and (c), just writing an equation is not sufficient for the "explanation" point. To earn credit, the student must connect the equation to issue to be explained.

Sample Student Response 1

a) ΔS° is negative for the reaction because ΔS is the measure of randomness or entropy or chaos. In a system, gases have more entropy than solids because gases have more freedom of movement. Thus, the reactants, which contain 3 gases are changed to products with a solid and 2 mols of gas, the ΔS decreases, becoming negative.

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

$= -145$

As the T increases, ΔG may become + because since ΔS is negative, then the factor $-T\Delta S$ is positive. Since spontaneous reactions have $\Delta G < 0$ and the Gibbs free energy equation is $\Delta G = \Delta H - T\Delta S$, then at a high enough T, the factor $-T\Delta G$ will be larger than ΔH & ΔG will be positive.

c) When ΔG goes from spontaneous to non spontaneous,

$\Delta G = 0$

$\Delta G = -RT\ln K$ As ΔG is becomes + and the equation

$0 = \ln K$ shifts to the left, the K will decrease

$K = 1$ because there will be less products.

d) At that point $\Delta G = 0$

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

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

$T\Delta S = \Delta H$

$$\boxed{T = \frac{\Delta H}{\Delta S}}$$

This equation only makes an approximate value because the ΔH and ΔS may change slightly at different temperatures. Yet for most practical purposes, they are constant.

Comment: Full credit is given for **part a** since the student correctly evaluates the change in disorder as the reactants are converted to products. In **part b**, the student appropriately discusses the Gibbs-Helmholtz equation and correctly notes how the two state functions will change as temperature is increased. The answer in **part c** could have been clearer; nonetheless, the answer does reflect an understanding of the relationship between temperature, K_{eq}, and free energy change, so both points were awarded. In **part d**, the student correctly notes that at the "change-over" point the free energy change becomes zero and that both changes in entropy and enthalpy are slightly temperature dependent. The total score for this answer was 8

Sample Student Response 2

(a) The sign of ΔS° would be + because the entropy is increasing. This can be observed if the number of moles are observed. There are 3 moles of molecules on the reactant side and 5 moles of molecules on the products side. This shows that the entropy is increasing because the state is becoming more disordered.

(b) ΔG° would decrease if the temperature were increased. If the equation: $\Delta G^\circ = \Delta H - T\Delta S$, is taken into account, then it can be seen that if the ΔS is positive, then an increase in temperature would lead to a decrease in ΔG.

(c) The reaction is exothermic since it is spontaneous at the given Temperature. Because the reaction is exothermic, and increase in the temperature would favor the reactants. Therefore, the reaction would shift towards the reactants.

(d) $\Delta G^\circ = \Delta H - T\Delta S$ can be used to determine the temperature at which the reaction becomes spontaneous. Just set $\Delta G^\circ = 0$ and plug in ΔH and ΔS. It is not exact because the ΔH changes along until the Temperature.

Comment: This paper earned 4 of the possible 8 points. No points were given in **part a**, because the student failed to recognize that changes in phase are more important in determining changes in entropy than changes in the number of moles of products versus the number of moles of reactants. Full credit was given in **part b**, since the analysis using the Gibbs-Helmholtz equation is correct using the incorrect sign of entropy change from **part a**. No points were awarded in **part c**, although there is some merit in the analysis of the exothermic nature of the reaction and the effect of increasing the temperature on the position of the equilibrium. In fact, the student did not answer the question, "What is the change in the value of the equilibrium constant?" Two points were awarded in **part d** for the correct use of the Gibbs-Helmholtz equation and the recognition that (at least) one of the state functions is dependent on temperature.

Question 7

The student's performance on this question is reflected in the liberal nature of the scoring standards. It seems that most students are not exposed appropriately to titration curves or taught the properties of polyprotic acids.

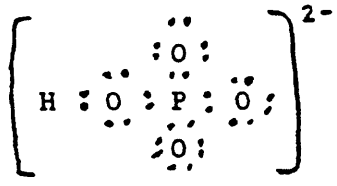
Scoring Standards

(a) $PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}$

$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$

} only *(2 pts.)*

Note: any proton transfer to any P_xO_y species earns 1 point.

(b) 

explicit 32 e^-
explicit 2 − charge (somewhere) *(2 pts.)*
not more than 1 double P-O bond

Note: HPO_4^{2-} (formula only) or other P_xO_y species with correct diagram earns 1 point.

(c) Graph goes from upper left to lower right (pH decreases) *(1 pt.)*

Two protons transferred { Two "buffers" / Two "equivalence" } in either direction *(1 pt.)*

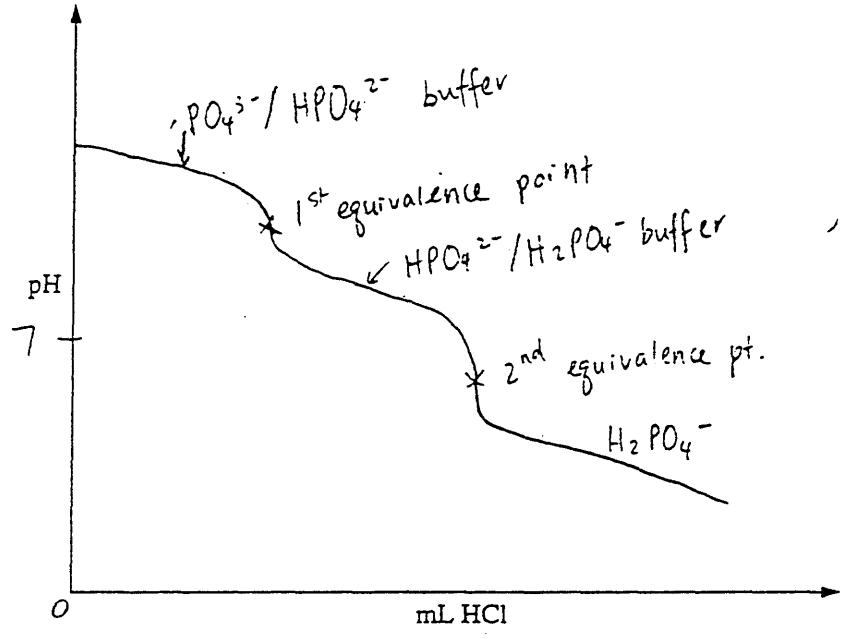
Explain/correctly label at least one "buffer" or "equivalence" region *(1 pt.)*

(d) $H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4$ *(1 pt.)*

Note: other proton transfer earns 1 point if consistent with product in part (a)

Sample Student Response 1

(c) Sketch a graph using the axes provided, showing the shape of the titration curve that results when 100. milliliters of the HCl solution is added slowly from a buret to the Na_3PO_4 solution. Account for the shape of the curve.



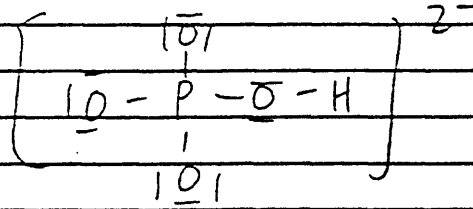
(d) Write the equation for the reaction that occurs if a few additional milliliters of the HCl solution are added to the solution resulting from the titration in (c).

$HPO_4^{2-} + H_2O \rightleftharpoons H_3PO_4 + OH^-$

7a) ① $H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-}$

② $H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$

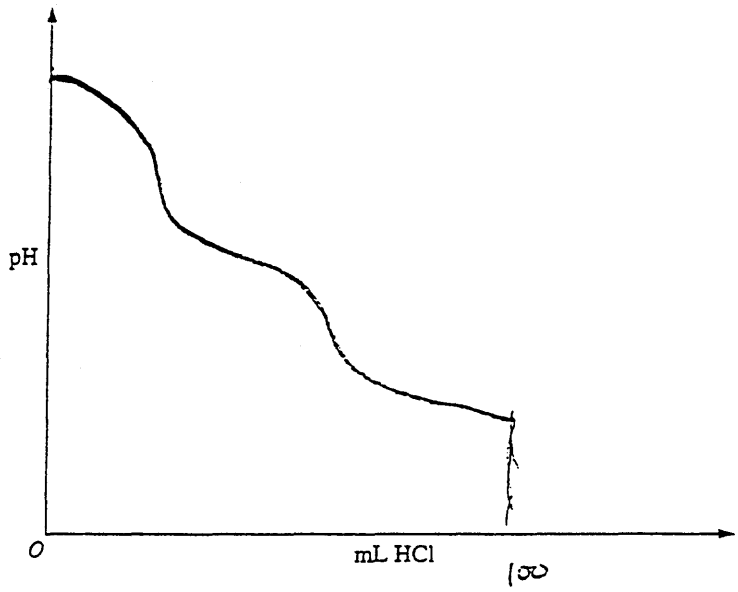
b) In ① HPO_4^{2-} acts both as Brönsted acid & base



c) $H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4$ (aq)

Comment: This was one of a very few perfect responses (a score of 8 points) to this question. Both points were clearly earned in **part a** and in **part b**. The nature of this student's titration curve (**part c**) reflects a real understanding of the nature of this system, the somewhat diffuse equivalence points, and the buffering regions. The response to **part d** is exactly right.

Sample Student Response 2



(d) Write the equation for the reaction that occurs if a few additional milliliters of the HCl solution are added to the solution resulting from the titration in (c).

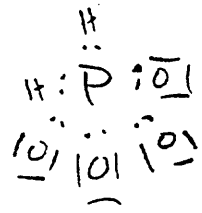
(a) $H^+ + PO_4^{3-} \rightarrow HPO_4^{2-}$

$H^+ + HPO_4^{2-} \rightarrow H_2PO_4^-$

(b) $H_2PO_4^-$

octahedral

6, 4, 0



(c) The shape of the curve is influenced by the formation of the chemicals that occurs. The pH of the solution drops each time a more powerful acid forms. Therefore, when HPO_4^{2-} forms, there is a drop, as well as when $H_2PO_4^-$ forms, where there is also a drop in the curve.

(d) $H_2PO_4^- + H^+ \rightarrow H_3PO_4$

Comment: The student clearly earns the two points in **part a**, but he or she fails to identify the amphoteric species, and the Lewis structure has little validity in reference to the octet rule. This student earns a point in **part c** for the shape of the titration curve and another point for identifying the equivalence points as "drops" occurring with the formation of each successive mole of acid. The student was also awarded a point in **part d** for correctly writing the appropriate equation for a total score of 5.

Question 8

This question gave the students an opportunity to relate chemical principles to everyday experiences. The attempt to make chemistry "relevant" has become more and more apparent in recent years and that trend is reflected in each of the four parts to this question.

Scoring Standards

(a) The addition of a solute lowers the freezing point of water. *(1 pt.)*

A mole of NaCl contains (dissociates into) 2 moles of ions/particles, whereas a mole of $CaCl_2$ contains (dissociates into) 3 moles of ions. Therefore $CaCl_2$ is more effective. *(1 pt.)*

(b) Hydrogen bonding is the most important intermolecular attractive force between molecules of H_2O and between molecules of NH_3. *(1 pt.)*

Water is a liquid because the hydrogen-bonding forces are stronger between adjacent H_2O molecules than between adjacent NH_3 molecules. *(1 pt.)*

Further explanations for the stronger hydrogen bonding in H_2O include the larger dipole moment (or more polar character) of H_2O compared to NH_3 and the fact that O is more electronegative than N is.

(c) Graphite's structure consists of 2-dimensional sheets of covalently bonded carbon atoms. The attractive forces between sheets (layers) are weak London (dispersion) forces, which allow the sheets to slide easily over one another. *(1 pt.)*

Note: must indicate *layers* and *sliding* to earn point.

Diamond consists of an extended 3-dimensional covalent network of carbon atoms. This makes diamond a very hard substance. *(1 pt.)*

(d) Vinegar, a dilute solution of acteic acid, reacts with the white solid, which contains metal carbonates, *(1 pt.)*

in a neutralization reaction to form gaseous CO_2. *(1 pt.)*

Sample Student Response 1

(a) When NaCl dissolves in water, the ions interfere among the water molecules and make them harder to crystalize. That would lower the freezing point of water and the ice would melt even at a temperature lower than 0°C. $CaCl_2$ may be more effective, because one mole of it produces 3 moles of ions while one mole of NaCl produced only 2 moles of ions. More the ions more the interference, so lower the freezing point.

(b) O is more electronegative than N. So the hydrogen bond among H_2O molecules and stronger than that in NH_3. The stronger intermolecular force makes H_2O a liquid, and the weaker intermolecular force in NH_3 makes it a gas.

(c) In graphite, the C atoms are arranged in layers. Those layers can slide on each other. That's why graphite can be used as a lubricant.
The structure of diamond is a huge covalent network of C atoms. It is very hard and has a very high melting point, so it is suitable for being an abrasive.

(d) The white residue is likely to contain some carbonates or bicarbonates. When vinegar, which is an acid, is added to these carbonates or bicarbonates, they react and form CO_2, which is the bubbles.

Comment: Since students were not required to relate freezing-point depression to vapor-pressure lowering, the statement that the added salt lowers the freezing point of water earned the first point in **part a**. The second point in this part was awarded for the clear recognition of the difference in the *i* factor for the two solutes. Mentioning hydrogen bonding and relating the strength of the hydrogen bonds in the two molecules to electronegativity in oxygen and nitrogen earned both points in **part b**. In **part c**, the response clearly earned the first point in explaining the lubricating properties of graphite as a function of sliding layers and, even though the three-dimensional nature of the covalent network was not mentioned, the second point was also awarded. The response to **part d** is right on the mark. The total score was 8 points.

Sample Student Response 2

(a) NaCl BREAKS INTO 2 ION WHERE $CaCl_2$ BREAKS INTO 3. FREEZING POINT DEPRESSION IS DEPENDANT ON THE # OF IONS MORE IONS ⇒ MORE FREEZ PT. DEP. AS THE FREZ. PT. IS REDUCED ICE MELTS.

(b) H_2O HAS MORE INTRAMOLECULAR ATTRACTIONS BECAUSE OF H BONDS.

(c) DIAMOND'S CARBONS ARE BONDED TETRAHEDRAL WHEREAS GRAPHITE'S ARE BONDED IN A PLANE. ALLOWING THE PLANES TO SLIDE OVER ONE ANOTHER AND THE CARBONS WHICH STICK BUT TO CHIP AWAY OTHER ATOMS.

(d) CH_3COOH IS A WEAK ACID. ACIDS CAUSE THE CO_3^{2-} ION TO FORM $CO_{2(g)}$ WHICH FIZZES / BUBBLES

Comment: Although the response is rather cryptic, since the student notes in **part a** that the freezing point is reduced by dissolved solutes and that calcium chloride produces more ions in solution than sodium chloride, the response earned both points. In **part b**, the student loses a point for mistakenly identifying hydrogen bonding as an intramolecular force and in **part c**, a point was deducted because the student failed to note the covalent network structure of diamond. In **part d**, the student gets back on track by concisely explaining the effervescence when vinegar is added to the white residue in a tea kettle.

Question 9

Atomic structure and chemical bonding, frequently the topics of essay questions on the AP Chemistry Examination, were the foci in this question. In addressing the four parts, students were required to relate differences in atomic size, crystal-lattice energy, and ionization energy to chemical principles. The fact that very few students scored well on **part b** is indicative, perhaps, that this topic is often glossed over in AP courses and should receive more attention.

Scoring Standards

(a) Ca^{2+} has fewer electrons, thus it is smaller than Ca *(1 pt.)*

The outermost electron in Ca is in a 4*s* orbital, whereas the outermost electron in Ca^{2+} in in a 3*p* orbital *(1 pt.)*

Note: The first point is earned for indicating the loss of electrons, the second point for indicating the outermost electrons are in different shells -- must account for the <u>magnitude</u> of the size difference between Ca and Ca^{2+}.

(b) *U* for CaO is more negative than *U* for K_2O, so it is more difficult to break up the CaO lattice (stronger bonds in CaO). *(1 pt.)*

Ca^{2+} is smaller than K^+, so internuclear separations (between cations and O^{2-})are less,

OR, *(1 pt.)*

Ca^{2+} is more highly charged than K^+, thus cation–O^{2-} bonds are stronger

Note: understanding what "lattice energy" is earns 1 point; size or charge explanation needed for the second point. Responses that use Lewis structures or otherwise indicate *molecules* rather than ionic lattice earn no points.

(c) (i) Ca has more protons and is smaller. The outermost electrons are more strongly held by the nuclear charge of Ca. *(1 pt.)*

(ii) The outermost electrons in Ca are in the 4*s*, which is a higher energy orbital (more shielded) than the 3*p* electron in K. *(1 pt.)*

Note: for (i), the idea of attraction between nucleus and electrons must be present; for (ii), a "noble-gas configuration" argument must be tied to an energy argument in order to earn credit.

(d) The highest energy (outermost) electron in Al is in a 3*p* orbital, whereas that electron in Mg is in a 3*s* orbital. *(1 pt.)*

The 3*p* electron in Al is of higher energy (is more shielded) than is the 3*s* electron in Mg. *(1 pt.)*

Note: noting that different orbitals are involved earns the first point; a correct energy argument earns the second point.

Responses that attribute the greater stability of Ca over K (or K^+ over Ca^+, or Mg over Al) to the stability of a completely filled (*vs.* half or partially filled) orbital earn NO credit.

Sample Student Response 1

(a) The electron configuration of Ca is $[Ar]4s^2$, while that of Ca^{2+} is [Ar]. Ca has electrons in the $n=4$ shell, while Ca^{2+} does not. Since this is the outermost shell, this explains the difference in the radii of the two species.

(b) By Coulomb's law, the lattice energy $\propto \frac{q_+ \cdot q_-}{r^2}$. Since CaO contains Ca^{2+} ions and O^{2-} ions, while K_2O contains K^+ ions (as opposed to Ca^{2+} ions) and O^{2-} ions, the lattice energy will be higher

(c) (i) The electron configuration of Ca is $[Ar]4s^2$ and K's electron configuration is $[Ar]4s^2$. Removing a 4s electron from Ca is harder than doing so from K. Since both are shielded by the same number of electrons, but Ca has more protons a more positive nucleus.

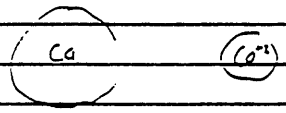
(ii) The second ionization energy of K is higher than that for Ca because it involves removing an electron from the $n=3$ shell, while for Ca it involves removing a $4s_1$ electron which is still shielded by inner orbitals.

The electron configuration of Al is $[Ne]3s^23p^1$. The first ionization energy involves removing the 3p electron. This is relatively easy to do because it is shielded by the 3s electrons. On the other hand, the e^- configuration of Mg is $[Ne]3s^2$ and the first ionization energy involves removing one of the 3s electrons, which is not shielded by its own orbital (3s).

Comment: Although the student does not specifically note that the calcium atom has more electrons than the calcium ion in **part a**, he or she clearly understands why the ion is smaller and therefore gets both points for this answer. In **part b**, relating the lattice energy to charge magnitude through Coulomb's law earns 2 points, even though there may be some confusion relative to the algebraic sign. In spite of the error in the electron configuration, it is clear – from **part c(ii)** – that the student knows potassium has only one 4*s* electron and understands that ionization energy is a function of nuclear charge. The answer in **part c(ii)** is right on the mark. The student who wrote this paper was one of a very few who invoked shielding correctly in the answer to **part d** and thus earned full credit (8 points).

Sample Student Response 2

(a) In the ion form, the atom has lost two electrons thus the central nucleus can pull on the atom more. This pull decreases the atomic radius.



(b) The formation of CaO requires more energy because one must ionize two electrons to combine with the oxygen molecule where in the K_2O crystal two seperate electrons in low 4s' orbitals must be ionized to form the crystal.

(c) In Ca, the first electron is being held in a stable 4s orbital that is filled. Therefore, the ionization of this first electron is high. In K, the electron is easily stripped away because the electron is in a unfilled 4s' spot.

The second ionization energy for Ca is lower than K's second because Cadium's second electron is in an unfilled 4s location. However, it is easier to ionize the first electron in K that is in the relatively same spot because K has less nucleus weight and attraction. The K second ionization level is very high because K has a filled 3p orbital where the next electron is being ionized from. This stability makes ionization difficult.

(d) The first ionization energy is higher for Mg because Mg has a stable filled 3s orbital while Al's first electron rests in an unfilled 3p orbital. Thus, although this breaks the general trend, the position of the electron to be ionized in Mg accounts for this difference.

Comment: This response earned 4 points. Both points in **part a** were given for noting that electrons are lost in the ionization while implying that the nuclear charge remains the same, increasing the force of attraction of the nucleus per electron. In **part b**, the student lost both points since it is clear he or she does not understand the nature of lattice energy. In **part c**, the student earned only 1 of the 2 points, for invoking a common error in responses to this question (that filled subshells are especially stable) in the first part. The point for **part c (ii)** was awarded since the student clearly knew that the second electron lost from potassium comes from a 3p orbital. In **part d**, a point was earned by noting the electron configurations of the species involved, but the explanation point was lost by using the same fallacious argument as in **part c**.

Chapter IV

Statistical Information

■ SECTION II SCORES

Table 4.1 shows the score distribution for the free-response section of the 1994 AP Chemistry Examination. Students were required to complete Questions 1, 4, and 5, and then had to choose a fourth question from Questions 2 and 3, and two more from Questions 6-9. Questions 1-3 were scored on a 9-point scale, Question 4 on a 15-point scale, and Questions 5-9 on an 8-point scale. For each question, the number of students at each score point is listed, along with the total number of candidates attempting that essay.

Question 2 had the highest mean as percent of maximum possible score, indicating that the score earned by this question's typical student was closer to the question's highest score than for any other question. Question 1 had the greatest standard deviation, indicating that the scores tended to be spread out more than for the other questions.

Table 4.1 — Section II Scores

Score	Question 1 (9)*	Question 2 (9)	Question 3 (9)	Question 4 (15)	Question 5 (8)	Question 6 (8)	Question 7 (8)	Question 8 (8)	Question 9 (8)
16									
15				215					
14				527					
13				710					
12				892					
11				1,226					
10				1,473					
9	1,532	357	800	1,740					
8	2,116	1,155	735	2,165	486	337	35	165	41
7	2,618	2,210	963	2,344	938	1,787	57	412	175
6	2,674	3,398	1,096	2,593	1,722	2,300	101	712	293
5	2,525	4,390	1,401	2,880	2,601	2,320	152	1,242	846
4	2,518	3,102	1,543	3,183	3,840	2,573	268	1,673	1,839
3	2,863	1,459	1,578	3,325	5,197	2,470	825	2,165	3,446
2	3,871	1,137	1,356	3,406	6,131	2,992	2,162	2,396	5,104
1	4,941	798	1,018	2,107	5,642	2,072	2,991	2,781	4,760
0	3,983	1,111	624	1,750	3,076	1,598	887	3,191	1,422
NR**	1,989	1,226	173	1,094	1,997	2,305	1,840	283	242
Number of Candidates	31,630	19,117	11,114	31,630	31,630	18,449	7,478	14,737	17,926
Standard Deviation	2.85	2.13	2.53	3.74	2.00	2.19	1.35	2.03	1.46
Mean	3.45	4.71	4.32	5.37	2.61	3.60	1.73	2.41	2.24
Mean as % of Max.	38	52	48	36	33	45	22	30	28

* Numbers in brackets indicate the maximum possible score.
** No response. Students gave either no response or a response not on the topic. Responses that fall into this category were not included in the calculation of number of candidates, mean, standard deviation, or means as a percentage of maximum.

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