

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

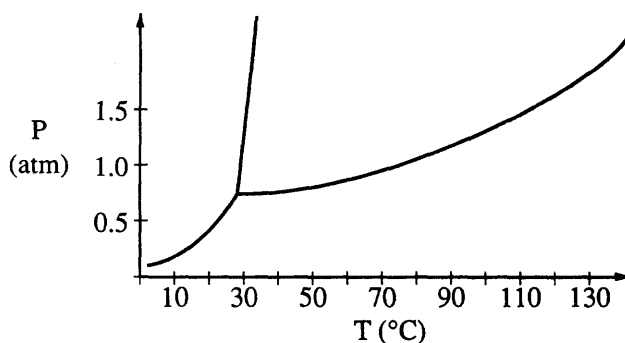
Directions: Each set of lettered choices below refers to the numbered questions or statements immediately following it. Select the one lettered choice that best answers each question or best fits each statement and then fill in the corresponding oval on the answer sheet. A choice may be used once, more 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

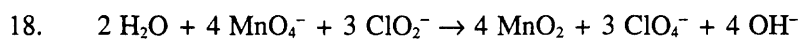
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Part B

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

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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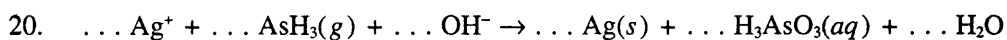


Which species acts as an oxidizing agent in the reaction represented above?

- (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

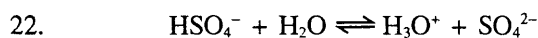


When the equation above is balanced with lowest whole-number coefficients, the coefficient for OH^- is

- (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



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

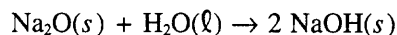
The proposed steps for a catalyzed reaction between Ce^{4+} and Tl^+ are represented above. The products of the overall catalyzed reaction are

- (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. $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(\ell) \quad \Delta H^\circ = -286 \text{ kJ}$
 $2 \text{Na}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{Na}_2\text{O}(s) \quad \Delta H^\circ = -414 \text{ kJ}$
 $\text{Na}(s) + \frac{1}{2} \text{O}_2(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{NaOH}(s) \quad \Delta H^\circ = -425 \text{ kJ}$

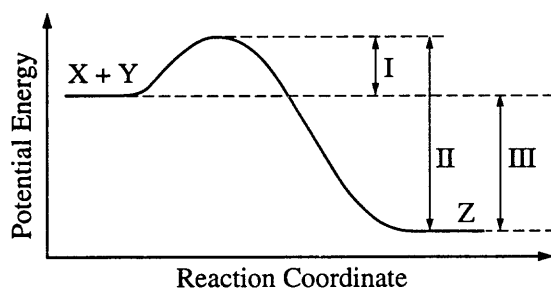
Based on the information above, what is the standard enthalpy change for the following reaction?



- (A) $-1,125 \text{ kJ}$
(B) -978 kJ
(C) -722 kJ
(D) -150 kJ
(E) $+275 \text{ kJ}$
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) $4, 2, 0, \frac{1}{2}$

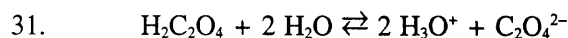
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28. Given that a solution is 5 percent sucrose by mass, what additional information is necessary to calculate the molarity of the solution?
- The density of water
 - The density of the solution
 - The molar mass of sucrose
- (A) I only
 (B) II only
 (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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Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, 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?

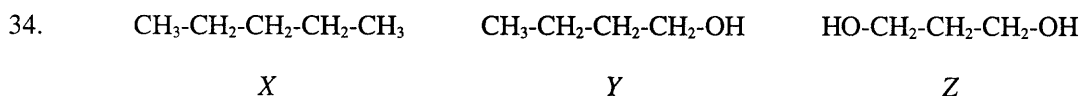
- (A) 5.36×10^{-2}
- (B) 5.3×10^{-5}
- (C) 2.8×10^{-6}
- (D) 1.9×10^{-10}
- (E) 1.9×10^{-13}

32. $\text{CH}_3\text{CH}_2\text{OH}$ 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}

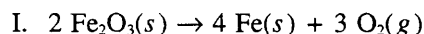
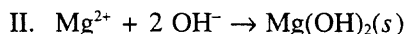


Based on concepts of polarity and hydrogen bonding, which of the following sequences correctly lists the compounds above in the order of their increasing solubility in water?

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

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



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

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

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° , 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 $\text{Zn}(\text{NO}_3)_2$, 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 $0.0821 \text{ (L} \cdot \text{atm)} / (\text{mol} \cdot \text{K})$.

- (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?

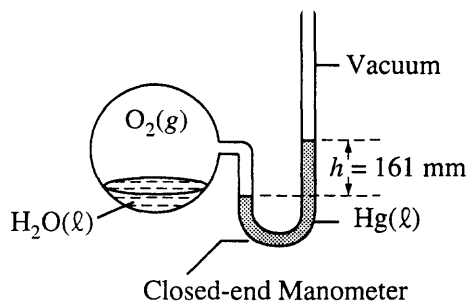
- I. There must be enough sample in the tube to cover the entire light path.
II. The instrument must be periodically reset using a standard.
III. The solution must be saturated.

- (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 $\text{O}_2(\text{g})$ 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) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$ and $\text{CH}_3\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—CH}_3$
- (B) $\text{CH}_3\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—CH}_3$ and $\text{CH}_3\text{—}\underset{\text{CH}_3}{\text{C}}\text{=CH}_2$
- (C) $\text{CH}_3\text{—O—CH}_3$ and $\text{CH}_3\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—CH}_3$
- (D) $\text{CH}_3\text{—OH}$ and $\text{CH}_3\text{—CH}_2\text{—OH}$
- (E) CH_4 and $\text{CH}_2\text{=CH}_2$
44. Which of the following solutions has the lowest freezing point?
- (A) $0.20 \text{ m C}_6\text{H}_{12}\text{O}_6$, glucose
 (B) $0.20 \text{ m NH}_4\text{Br}$
 (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?
- The average molecular mass of the gas
 - The average distance between the molecules
 - 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. $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g) + \text{energy}$
- 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?
- Decreasing the volume of the container
 - Raising the temperature
 - 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. $4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$
- 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?
- $[\text{HCl}]$ must be less than $[\text{Cl}_2]$.
 - $[\text{O}_2]$ must be greater than $[\text{HCl}]$.
 - $[\text{Cl}_2]$ must equal $[\text{H}_2\text{O}]$.
- (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, $\text{Ca}(\text{OH})_2$, 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, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
 (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?
- | <u>$[\text{K}^+]$</u> | <u>$[\text{SO}_4^{2-}]$</u> |
|----------------------------------|--|
| (A) 0.020 <i>M</i> | 0.020 <i>M</i> |
| (B) 1.0 <i>M</i> | 2.0 <i>M</i> |
| (C) 2.0 <i>M</i> | 1.0 <i>M</i> |
| (D) 2.0 <i>M</i> | 2.0 <i>M</i> |
| (E) 4.0 <i>M</i> | 2.0 <i>M</i> |
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 $\text{Ba}(\text{OH})_2$?
- (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.
$$\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$$
- 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.

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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. $\text{I}_2(g) + 3 \text{Cl}_2(g) \rightarrow 2 \text{ICl}_3(g)$

According to the data in the table below, what is the value of ΔH° 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) $\text{Al}_2(\text{SO}_4)_3$
(B) $(\text{NH}_4)_2\text{SO}_4$
(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

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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. $\dots \text{Fe}(\text{OH})_2 + \dots \text{O}_2 + \dots \text{H}_2\text{O} \rightarrow \dots \text{Fe}(\text{OH})_3$
- If 1 mole of O_2 oxidizes $\text{Fe}(\text{OH})_2$ according to the reaction represented above, how many moles of $\text{Fe}(\text{OH})_3$ can be formed?
- (A) 2
 - (B) 3
 - (C) 4
 - (D) 5
 - (E) 6

GO ON TO THE NEXT PAGE 

72. The nuclide $^{249}_{96}\text{Cm}$ is radioactive and decays by the loss of one beta (β^-) particle. The product nuclide is
- (A) $^{245}_{94}\text{Pu}$
 (B) $^{245}_{95}\text{Am}$
 (C) $^{248}_{96}\text{Cm}$
 (D) $^{250}_{96}\text{Cm}$
 (E) $^{249}_{97}\text{Bk}$
73. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
- 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 $\text{Ca}(\text{OH})_2$ 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.

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.



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.

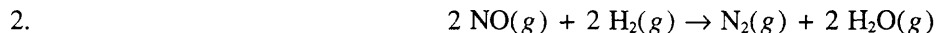
- (a) Write the expression for the solubility-product constant, K_{sp} , and calculate its value at 18°C .
- (b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 liter of saturated MgF_2 solution at 18°C to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the 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 $\text{Mg}(\text{NO}_3)_2$ 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.



GO ON TO THE NEXT PAGE

Part B
(20 percent)

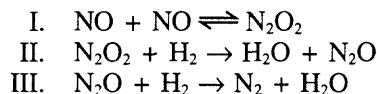
Solve EITHER problem 2 OR problem 3 in this part. (A second problem will not be scored.)



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)		Initial Rate of Formation of N_2 (mol/L·min)
	[NO]	[H ₂]	
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}

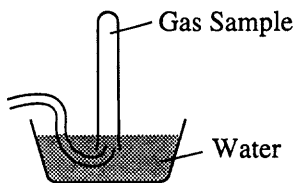
- (a) (i) Determine the order for each of the reactants, NO and H₂, from the data given and show your reasoning.
(ii) Write the overall rate law for the reaction.
- (b) Calculate the value of the rate constant, k, for the reaction. Include units.
- (c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H₂ had been consumed.
- (d) The following sequence of elementary steps is a proposed mechanism for the reaction.



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.

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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 ₂ O (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, H₂ or H₂O, deviates more from ideal behavior? Explain your answer.

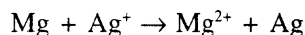
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Part C
(15 percent)

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.



- (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 

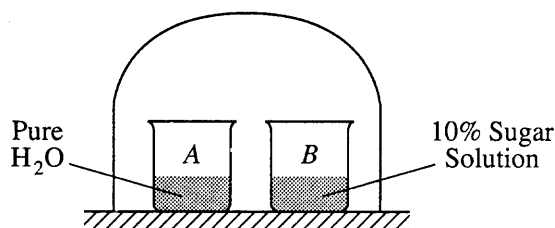
Part D
(45 percent)

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.

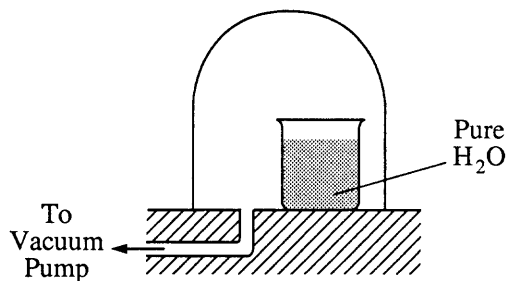
ANSWER THE FOLLOWING ESSAY QUESTION.

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.

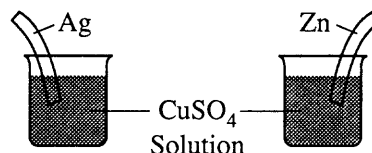
- (a) As the system shown on the right approaches equilibrium, what change occurs to the volume of water in beaker A? What happens to the concentration of the sugar solution in beaker B? Explain why these changes occur.



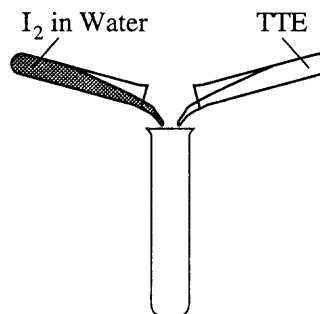
- (b) A bell jar connected to a vacuum pump is shown on the right. As the air pressure under the bell jar decreases, what behavior of water in the beaker will be observed? Explain why this occurs.



- (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.

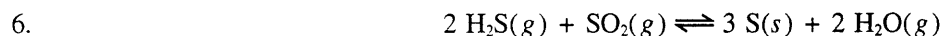


- (d) A water solution of I_2 is shaken with an equal volume of a nonpolar solvent such as TTE (trichlorotrifluoroethane). Describe the appearance of this system after shaking. (A diagram may be helpful.) Account for this observation.



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



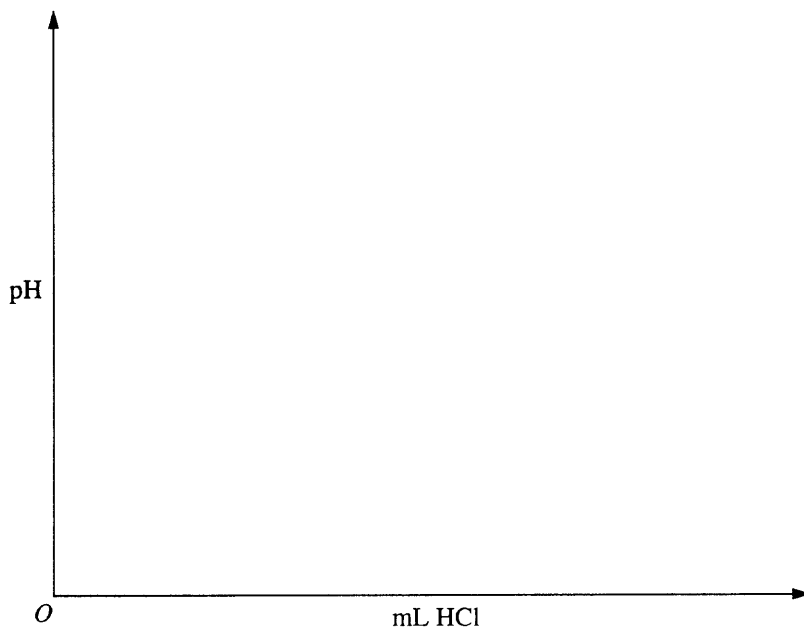
At 298 K, the standard enthalpy change, ΔH° , for the reaction represented above is -145 kilojoules.

- (a) Predict the sign of the standard entropy change, ΔS° , 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 ΔG° 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?

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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 Brønsted acid and as a Brønsted 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).

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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.

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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 $\text{CaO}(s)$ is $-3,460$ kilojoules per mole; the lattice energy for $\text{K}_2\text{O}(s)$ 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

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
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)

†Actinide Series:

GO ON TO THE NEXT PAGE

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

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

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 = $2.998 \times 10^8 \text{ m/sec}$

$\ln_e = 2.303 \log_{10}$

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

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

Avogadro's number = $6.022 \times 10^{23} \text{ molecules/mole}$

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

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

$\text{Li}^+ + \text{e}^-$	$\longrightarrow$	Li(s)	-3.05
$\text{Cs}^+ + \text{e}^-$	$\longrightarrow$	Cs(s)	-2.92
$\text{K}^+ + \text{e}^-$	$\longrightarrow$	K(s)	-2.92
$\text{Rb}^+ + \text{e}^-$	$\longrightarrow$	Rb(s)	-2.92
$\text{Ba}^{2+} + 2\text{e}^-$	$\longrightarrow$	Ba(s)	-2.90
$\text{Sr}^{2+} + 2\text{e}^-$	$\longrightarrow$	Sr(s)	-2.89
$\text{Ca}^{2+} + 2\text{e}^-$	$\longrightarrow$	Ca(s)	-2.87
$\text{Na}^+ + \text{e}^-$	$\longrightarrow$	Na(s)	-2.71
$\text{Mg}^{2+} + 2\text{e}^-$	$\longrightarrow$	Mg(s)	-2.37
$\text{Be}^{2+} + 2\text{e}^-$	$\longrightarrow$	Be(s)	-1.70
$\text{Al}^{3+} + 3\text{e}^-$	$\longrightarrow$	Al(s)	-1.66
$\text{Mn}^{2+} + 2\text{e}^-$	$\longrightarrow$	Mn(s)	-1.18
$\text{Zn}^{2+} + 2\text{e}^-$	$\longrightarrow$	Zn(s)	-0.76
$\text{Cr}^{3+} + 3\text{e}^-$	$\longrightarrow$	Cr(s)	-0.74
$\text{Fe}^{2+} + 2\text{e}^-$	$\longrightarrow$	Fe(s)	-0.44
$\text{Cr}^{3+} + \text{e}^-$	$\longrightarrow$	Cr^{2+}	-0.41
$\text{Cd}^{2+} + 2\text{e}^-$	$\longrightarrow$	Cd(s)	-0.40
$\text{Tl}^+ + \text{e}^-$	$\longrightarrow$	Tl(s)	-0.34
$\text{Co}^{2+} + 2\text{e}^-$	$\longrightarrow$	Co(s)	-0.28
$\text{Ni}^{2+} + 2\text{e}^-$	$\longrightarrow$	Ni(s)	-0.25
$\text{Sn}^{2+} + 2\text{e}^-$	$\longrightarrow$	Sn(s)	-0.14
$\text{Pb}^{2+} + 2\text{e}^-$	$\longrightarrow$	Pb(s)	-0.13
$2\text{H}^+ + 2\text{e}^-$	$\longrightarrow$	$\text{H}_2(\text{g})$	0.00
$\text{S(s)} + 2\text{H}^+ + 2\text{e}^-$	$\longrightarrow$	H_2S	0.14
$\text{Sn}^{4+} + 2\text{e}^-$	$\longrightarrow$	Sn^{2+}	0.15
$\text{Cu}^{2+} + \text{e}^-$	$\longrightarrow$	Cu^+	0.15
$\text{Cu}^{2+} + 2\text{e}^-$	$\longrightarrow$	Cu(s)	0.34
$\text{Cu}^+ + \text{e}^-$	$\longrightarrow$	Cu(s)	0.52
$\text{I}_2(\text{s}) + 2\text{e}^-$	$\longrightarrow$	2I^-	0.53
$\text{Fe}^{3+} + \text{e}^-$	$\longrightarrow$	Fe^{2+}	0.77
$\text{Hg}_2^{2+} + 2\text{e}^-$	$\longrightarrow$	$2\text{Hg}(\text{ℓ})$	0.79
$\text{Ag}^+ + \text{e}^-$	$\longrightarrow$	Ag(s)	0.80
$\text{Hg}_2^{2+} + 2\text{e}^-$	$\longrightarrow$	$\text{Hg}(\text{ℓ})$	0.85
$2\text{Hg}^{2+} + 2\text{e}^-$	$\longrightarrow$	Hg_2^{2+}	0.92
$\text{Br}_2(\text{ℓ}) + 2\text{e}^-$	$\longrightarrow$	2Br^-	1.07
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$	$\longrightarrow$	$2\text{H}_2\text{O}$	1.23
$\text{Cl}_2(\text{g}) + 2\text{e}^-$	$\longrightarrow$	2Cl^-	1.36
$\text{Au}^{3+} + 3\text{e}^-$	$\longrightarrow$	Au(s)	1.50
$\text{Co}^{3+} + \text{e}^-$	$\longrightarrow$	Co^{2+}	1.82
$\text{F}_2(\text{g}) + 2\text{e}^-$	$\longrightarrow$	2F^-	2.87

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APPENDIX - ANSWERS

AP CHEMISTRY 1994

Multiple-choice key transcribed from the matching supplied source.

Question	Answer	Question	Answer	Question	Answer
1	C	26	C	51	D
2	E	27	C	52	B
3	B	28	E	53	E
4	A	29	A	54	D
5	A	30	D	55	C
6	B	31	C	56	B
7	B	32	D	57	A
8	C	33	C	58	B
9	C	34	E	59	D
10	D	35	D	60	B
11	C	36	C	61	B
12	D	37	D	62	A
13	A	38	C	63	B
14	C	39	C	64	D
15	E	40	C	65	A
16	B	41	D	66	D
17	D	42	D	67	E
18	E	43	A	68	A
19	B	44	E	69	C
20	D	45	C	70	A
21	D	46	E	71	C
22	E	47	D	72	E
23	B	48	A	73	A
24	C	49	B	74	A
25	D	50	E	75	B

Optional FRQs retain the original exam selection instructions.

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

$$\begin{aligned} \text{(a)} \quad K_{sp} &= [\text{Mg}^{2+}][\text{F}^-]^2 && (1 \text{ pt.}) \\ &= (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 \\ &= 7.09 \times 10^{-9} && (1 \text{ pt.}) \end{aligned}$$

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.

$$\begin{aligned} \text{(b)} \quad K_{sp} &= [\text{Mg}^{2+}](2x + 0.100)^2 && 2x \ll 0.100 && (1 \text{ pt.}) \text{ for proper substitution} \\ 7.09 \times 10^{-9} &= [\text{Mg}^{2+}](0.100)^2 \\ [\text{Mg}^{2+}] &= (7.09 \times 10^{-9})/(10^{-2}) \\ &= 7.09 \times 10^{-7} \text{ M} && (1 \text{ pt.}) \end{aligned}$$

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

$$\begin{aligned} \text{(c)} \quad [\text{Mg}^{2+}]: \quad 100.0 \times 3.00 \times 10^{-3} &= 300.0 \times [\text{Mg}^{2+}] \\ [\text{Mg}^{2+}] &= 1.00 \times 10^{-3} \text{ M} \\ [\text{F}^-]: \quad 200.0 \times 2.00 \times 10^{-3} &= 300.0 \times [\text{F}^-] \\ [\text{F}^-] &= 1.33 \times 10^{-3} \text{ M} \end{aligned} \quad \left. \vphantom{\begin{aligned} [\text{Mg}^{2+}]: \\ [\text{F}^-]: \end{aligned}} \right\} \begin{array}{l} (1 \text{ pt.}) \text{ if } \underline{\text{both}} \\ \text{concentrations are} \\ \text{correct} \end{array}$$

$$\begin{aligned} Q = \text{Ion Product} &= [\text{Mg}^{2+}][\text{F}^-]^2 \\ &= (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 \quad ** \\ &= 1.77 \times 10^{-9} && (1 \text{ pt.}) \end{aligned}$$

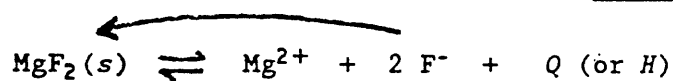
Since $Q < K_{sp}$, no precipitate will form (1 pt.)

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 exothermic

(1 pt.)



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.)

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 $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$, then $[\text{N}_2\text{O}_2] = [\text{NO}]^2$ and lost a point as a result.

Scoring Standards

- (a) (i) From exps. 1 and 2: Doubling $[\text{H}_2]$ while keeping $[\text{NO}]$ constant doubles the rate, therefore the reaction is *first order* in $[\text{H}_2]$. (1 pt.) for order and justification

From exps. 3 and 4: Doubling $[\text{NO}]$ while keeping $[\text{H}_2]$ constant quadruples the rate, therefore the reaction is *second order* in $[\text{NO}]$. (1 pt.) for order and justification

(ii) $\text{Rate} = k[\text{H}_2][\text{NO}]^2$ (1 pt.)

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

(b) $k = \frac{\text{Rate}}{[\text{H}_2][\text{NO}]^2}$

From exp. 1: $k = \frac{1.8 \times 10^{-4} \text{ M/min}}{(1.0 \times 10^{-3} \text{ M})(6.0 \times 10^{-3} \text{ M})^2}$ (1 pt.) for value
 $= 5.0 \times 10^3 \text{ M}^{-2} \text{ min}^{-1}$ (1 pt.) for units

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

- (c) Stoichiometry: $\text{NO}:\text{H}_2$ is 1:1

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

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

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

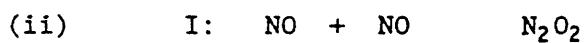
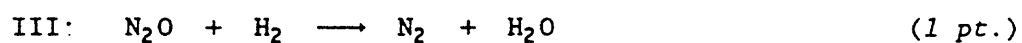
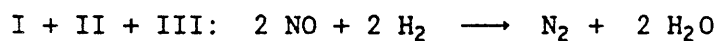
For II: $Rate = k[H_2][N_2O_2]$

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

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

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

Step II is the rate-determining step. (1 pt.)



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

$$(a) \quad n = \frac{PV}{RT} = \frac{(721)(0.090)}{(62.4)(298)} = 3.49 \times 10^{-3} \text{ mol H}_2$$

$25^\circ\text{C} \longrightarrow 298 \text{ K}$
 $745 - 24 = 721 \text{ mm Hg}$
 calculation of moles of H_2

(1 pt.)
 (1 pt.)
 (1 pt.)

$$(b) \quad \frac{(23.8)(0.090)}{(62.4)(298)} = 1.15 \times 10^{-4} \text{ mol H}_2\text{O} \quad (1 \text{ pt.})$$

$$(1.15 \times 10^{-4})(6.03 \times 10^{23}) = 6.92 \times 10^{19} \text{ molecules H}_2\text{O} \quad (1 \text{ pt.})$$

(c) The average kinetic energies are equal, so

$$\left(\frac{1}{2}mv^2\right)_{\text{H}_2\text{O}} = \left(\frac{1}{2}mv^2\right)_{\text{H}_2}$$

$$\frac{v_{\text{H}_2}}{v_{\text{H}_2\text{O}}} = \sqrt{\frac{MM_{\text{H}_2\text{O}}}{MM_{\text{H}_2}}} = \sqrt{\frac{18}{2}} = 3$$

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

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

(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.)

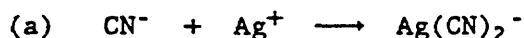
Question 4

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:

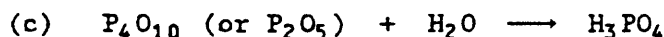
- 1) Each reaction is worth a total of 3 points
- 2) Reactants +1 point; products +2 points
- 3) Ignore balancing and states
- 4) Inappropriate ionization - maximum 1 point penalty per equation



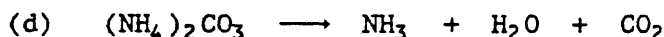
Note: any complex ion of Ag with cyanide with consistent charge earns 3 points;
AgCN given as product earns 1 product point



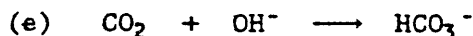
Note: If Mg used instead of Mn, maximum possible score is 2 points



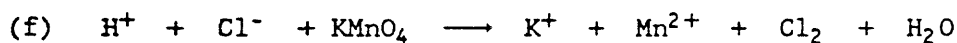
Note: Acidic species (H^+ or oxyacid of phosphorus) earns 1 product point;
P in +5 oxidation state in oxyanion earns 1 product point;
anions of oxyacids of phosphorus require H^+ for full credit
for products



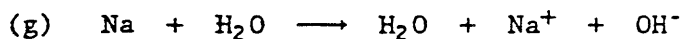
Note: Any one product earns 1 point; all three earns 2 product points
 $\text{NH}_4\text{OH} + \text{CO}_2$ earns 1 product point
 $\text{NH}_3 + \text{H}_2\text{CO}_3$ earns 1 product point



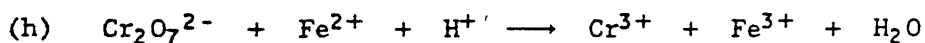
Note: $\text{CO}_3^{2-} + \text{H}_2\text{O}$ as products earns 2 product points
 CO_3^{2-} alone as product earns 1 product point
 $\text{HCO}_3^- + \text{H}_2\text{O}$ earns 1 product point



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



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



Note: All three products earns 2 product points
 Any valid redox product earns 1 product point
 H_2O only earns no credit
 If $\text{Cl}^- \rightarrow \text{Cl}_2$ instead of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, then maximum of 2 points possible

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.

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 $\rightarrow$ 2 moles of gas plus solid,
(3 moles $\rightarrow$ 2 moles earns no points)

OR,

2 gases $\rightarrow$ 1 gas + solid, (1 pt.)

OR,

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

Note: If statement is that ΔS^0 is positive, then explanation of
3 moles gas $\rightarrow$ 5 moles of gas earns 1 point
(3 moles $\rightarrow$ 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 $\rightarrow$ 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

$$\Delta G^0 = -RT \ln K_{eq} \quad (\text{or } \ln(K_1/K_2) = \Delta H^0/R(1/T_2 - 1/T_1))$$

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 $T = \Delta H^0/\Delta S^0$.
($\Delta G^0 = \Delta H^0 - T\Delta S^0$ is NOT sufficient without $\Delta G^0 = 0$.)

(1 pt.)

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.

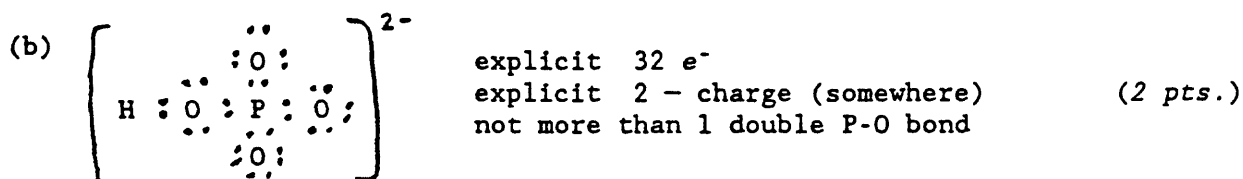
Question 7

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



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



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 $\left\{ \begin{array}{l} \text{Two "buffers"} \\ \text{Two "equivalence"} \end{array} \right\}$ in either direction (1 pt.)

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



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

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 acetic acid, reacts with the white solid, which contains metal carbonates, (1 pt.)
in a neutralization reaction to form gaseous CO_2 . (1 pt.)

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) Ca²⁺ has fewer electrons, thus it is smaller than Ca (1 pt.)

The outermost electron in Ca is in a 4s orbital, whereas the outermost electron in Ca²⁺ is in a 3p 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 magnitude of the size difference between Ca and Ca²⁺.

- (b) U for CaO is more negative than U for K₂O, so it is more difficult to break up the CaO lattice (stronger bonds in CaO). (1 pt.)

Ca²⁺ is smaller than K⁺, so internuclear separations (between cations and O²⁻) are less,

OR, (1 pt.)

Ca²⁺ is more highly charged than K⁺, thus cation-O²⁻ 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 4s, which is a higher energy orbital (more shielded) than the 3p 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 3p orbital, whereas that electron in Mg is in a 3s orbital. (1 pt.)

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