



Montogue

# AP Chemistry

## 60+7 Practice Problems

Lucas Monteiro Nogueira

### SECTION I



**No calculators  
allowed!**

1. Which of the following represents the correct electron configuration for the zinc ion,  $Zn^{2+}$ ?

- (A)  $[Ar]3d^{10}$
- (B)  $[Ar]4s^23d^8$
- (C)  $[Ar]4s^24d^8$
- (D)  $[Kr]4s^23d^8$

2. Arrange the following atoms in order of increasing atomic size.

Cl	Se	S
Chlorine	Selenium	Sulfur

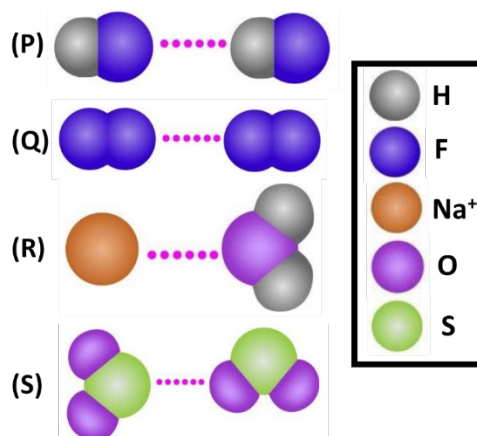
- (A)  $Cl < S < Se$
- (B)  $S < Cl < Se$
- (C)  $S < Se < Cl$
- (D)  $Se < S < Cl$

3. Arrange the following atoms in order of increasing first ionization energy,  $IE_1$ .

As	Sn	Sb
Arsenic	Tin	Antimony

- (A)  $As < Sn < Sb$
- (B)  $As < Sb < Sn$
- (C)  $Sb < Sn < As$
- (D)  $Sn < Sb < As$

Questions 4 and 5  
refer to the following diagram.



4. The figure illustrates different types of intermolecular attractive forces. Which of the following correctly defines the intermolecular attractions  $P$  to  $S$ ?

- (A)  $P$ . Hydrogen bond;  $Q$ . Dispersion force;  $R$ . Dipole-dipole;  $S$ . Dipole-dipole;
- (B)  $P$ . Hydrogen bond;  $Q$ . Dispersion force;  $R$ . Ion-dipole;  $S$ . Dipole-dipole;

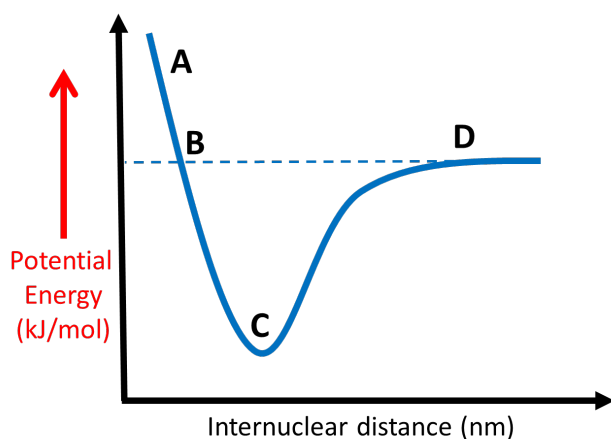
(C) P. Dispersion force; Q. Dipole-dipole; R. Ion-dipole; S. Dipole-dipole;

(D) P. Hydrogen bond; Q. Dipole-dipole; R. Ion-dipole; S. Dispersion force;

5. Which of the interactions in the previous illustration is the weakest?

- (A) P
- (B) Q
- (C) R
- (D) S

6. The following graph shows the amount of potential energy between two hydrogen atoms as the distance between them changes. At which point in the graph would a molecule of  $H_2$  be the most stable?



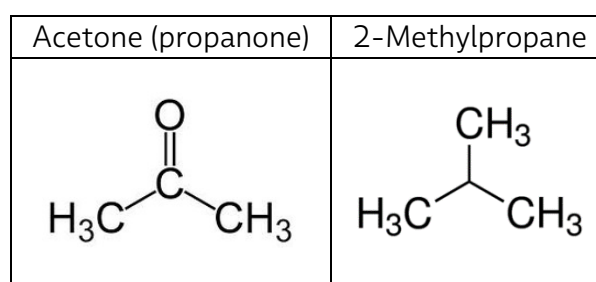
- (A) Point A
- (B) Point B
- (C) Point C
- (D) Point D

7. Which of the following properties indicates very strong intermolecular forces in a liquid?

- (A) Very low surface tension.
- (B) Very low critical temperature.
- (C) Very low boiling point.
- (D) Very low vapor pressure.

8. The nature of intermolecular forces achieved by certain molecules can be used to suggest qualitative trends in boiling points. With this concept in mind, which of the following is **false**?

- (A) Methanol,  $CH_3OH$ , boils at a greater temperature than methanethiol,  $CH_3SH$ , because only the former forms hydrogen bonds.
- (B) Acetone (shown below) boils at a greater temperature than 2-methylpropane (shown below) because acetone forms hydrogen bonds with other acetone molecules.



- (C) Xenon is a liquid at atmospheric temperature and 120 K, whereas argon is a gas under the same conditions. The reason is that a sample of Xe is held together by stronger dispersion forces than those that maintain a sample of Ar.
- (D) The boiling point of chlorine gas,  $Cl_2$ , is higher than that of krypton, Kr, because  $Cl_2$  is more polarizable and hence produces stronger dispersion forces than those that maintain krypton.

9. Rank the molecules  $NH_3$ ,  $NF_3$  and  $BF_3$  in increasing order of polarity (i.e., intensity of resultant dipole moment).

- (A)  $NF_3 < NH_3 < BF_3$
- (B)  $BF_3 < NF_3 < NH_3$
- (C)  $BF_3 < NH_3 < NF_3$
- (D)  $NF_3 < BF_3 < NH_3$

10. The total number of lone pairs of electrons in  $I_3^-$  is:

- (A) Zero
- (B) 3
- (C) 6
- (D) 9

- 11.** In the molecules  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ ,
- (A) The bond angles are the same.  
 (B) The bond lengths are the same.  
 (C) The hybridizations are the same.  
 (D) The molecular geometries are the same.

- 12.** Among the following four molecules, which ones have a planar structure?

$\text{CO}_3^{2-}$	$\text{SO}_3$
$\text{XeO}_3$	$\text{NO}_3^-$

- (A)  $\text{CO}_3^{2-}$ ,  $\text{SO}_3$ ,  $\text{XeO}_3$   
 (B)  $\text{SO}_3$ ,  $\text{XeO}_3$ ,  $\text{NO}_3^-$   
 (C)  $\text{CO}_3^{2-}$ ,  $\text{XeO}_3$ ,  $\text{NO}_3^-$   
 (D)  $\text{CO}_3^{2-}$ ,  $\text{SO}_3$ ,  $\text{NO}_3^-$

**Questions 13 to 16**

refer to the following molecules and ions.

$\text{CO}_2$	$\text{NO}_2^-$
$\text{CO}_3^{2-}$	$\text{NO}_3^-$

- 13.** Which molecule would have the shortest bonds?

- (A)  $\text{CO}_2$   
 (B)  $\text{CO}_3^{2-}$   
 (C)  $\text{NO}_2^-$   
 (D)  $\text{NO}_3^-$

- 14.** Which molecules are best represented by multiple resonance structures?

- (A)  $\text{CO}_2$  and  $\text{CO}_3^{2-}$   
 (B)  $\text{NO}_2^-$  and  $\text{NO}_3^-$   
 (C)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$   
 (D)  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$

- 15.** Which molecules exhibit  $sp^2$  hybridization around the central atom?

- (A)  $\text{CO}_2$  and  $\text{CO}_3^{2-}$   
 (B)  $\text{NO}_2^-$  and  $\text{NO}_3^-$   
 (C)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$   
 (D)  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$

- 16.** Which molecule would have the smallest bond angle between terminal atoms?

- (A)  $\text{CO}_2$   
 (B)  $\text{CO}_3^{2-}$   
 (C)  $\text{NO}_2^-$   
 (D)  $\text{NO}_3^-$

- 17.** What is the value of the compressibility factor of an ideal gas?

- (A) 1.0  
 (B) 1.5  
 (C) 2.0  
 (D)  $\infty$

- 18.** Barium carbonate is a white salt that occurs naturally as the mineral witherite. Assuming full decomposition, the volume of  $\text{CO}_2$  released at STP upon heating 98.5 g of  $\text{BaCO}_3$  is:

- (A) 5.6 L  
 (B) 11.2 L  
 (C) 16.8 L  
 (D) 22.4 L

- 19.** What volume of hydrogen gas at  $25^\circ\text{C}$  and 1 atm is necessary to produce 32.4 g of elemental boron from the reduction of boron trichloride?

- (A)  $\frac{4.5 \times 0.082 \times 25}{1.0}$  L  
 (B)  $\frac{6.0 \times 0.082 \times 25}{1.0}$  L  
 (C)  $\frac{4.5 \times 0.082 \times 298}{1.0}$  L  
 (D)  $\frac{6.0 \times 0.082 \times 298}{1.0}$  L

- 20.** A 3-liter gas mixture of propane ( $\text{C}_3\text{H}_8$ ) and butane ( $\text{C}_4\text{H}_{10}$ ) underwent complete combustion at  $25^\circ\text{C}$  to yield 10 liters of carbon dioxide. Which of the following is the original composition of the gas mixture?

- (A) 1 liter of  $\text{C}_3\text{H}_8$  and 2 liters of  $\text{C}_4\text{H}_{10}$   
 (B) 2 liters of  $\text{C}_3\text{H}_8$  and 1 liter of  $\text{C}_4\text{H}_{10}$   
 (C) 1.5 liters of  $\text{C}_3\text{H}_8$  and 2.5 liters of  $\text{C}_4\text{H}_{10}$   
 (D) 2.5 liters of  $\text{C}_4\text{H}_{10}$  and 1.5 liters of  $\text{C}_3\text{H}_8$

21. 2 g of gaseous  $\text{H}_2$  reacts with 24 g of gaseous  $\text{O}_2$  to form water. How much water is formed?

- (A) 10.8 g
- (B) 13.5 g
- (C) 18 g
- (D) 27 g

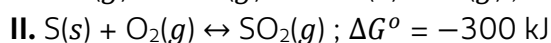
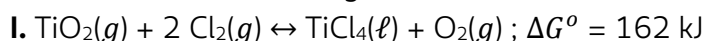
22. Which of the following species has zero standard molar enthalpy of formation?

- (A)  $\text{Br}_2(g)$
- (B)  $\text{Cl}_2(g)$
- (C)  $\text{H}_2\text{O}(g)$
- (D)  $\text{CH}_4(g)$

23. Which of the following changes has the sign of  $\Delta S$  (positive or negative) opposite to that of the other three?

- (A)  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$
- (B)  $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(\ell)$
- (C)  $\text{F}_2(\ell) \rightarrow \text{F}_2(g)$
- (D)  $\text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g)$

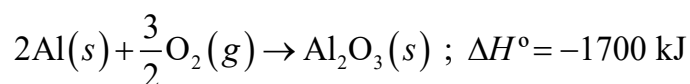
24. Consider the following two reactions at 298 K.



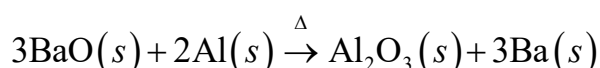
Which of the following is true?

- (A) Reactions I and II are spontaneous.
- (B) Reaction I is spontaneous, but reaction II is not.
- (C) Reaction II is spontaneous, but reaction I is not.
- (D) Neither reaction is spontaneous.

25. Barium metal is produced by the reaction of aluminum with barium oxide. From the standard reaction enthalpies,



calculate the reaction enthalpy for the production of metallic barium in the reaction



- (A)  $-150 \text{ kJ}$
- (B)  $-50 \text{ kJ}$
- (C)  $+50 \text{ kJ}$
- (D)  $+150 \text{ kJ}$

26. The standard heat of formation of  $\text{HI}(g)$  is 27 kJ. The bond dissociation energies of H–H and H–I are 440 kJ and 300 kJ, respectively. Using these data, what is the bond dissociation energy of a I–I bond?

- (A) 95 kJ
- (B) 107 kJ
- (C) 214 kJ
- (D) 247 kJ

27. The following kinetic data refer to the hypothetical reaction  $2\text{A} + \text{B}_2 \rightarrow 2\text{AB}$ .

[A] (mol L <sup>-1</sup> )	[B <sub>2</sub> ] (mol L <sup>-1</sup> )	Rate (mol L <sup>-1</sup> min <sup>-1</sup> )
1.0	2.0	$4 \times 10^{-3}$
2.0	2.0	$8 \times 10^{-3}$
1.0	4.0	$1.6 \times 10^{-2}$

The orders of reaction with respect to A and B<sub>2</sub> are, respectively:

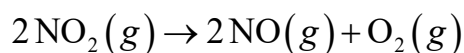
- (A) 1 and 1
- (B) 1 and 2
- (C) 2 and 1
- (D) 2 and 2

28. A reaction was observed for 60 minutes. Every 10 minutes, the percent of reactant remaining was measured. According to the data in the following table, which of the following most accurately describes the reaction order and half-life of this reaction?

Time (min)	Reactant remaining (g)
0	120
10	94
20	73
30	58
40	44
50	34
60	26

	Reaction order	Half-life (min)
(A)	1st	28
(B)	2nd	51
(C)	1st	28
(D)	2nd	51

**29.** The rate constant for the decomposition of nitrogen dioxide,



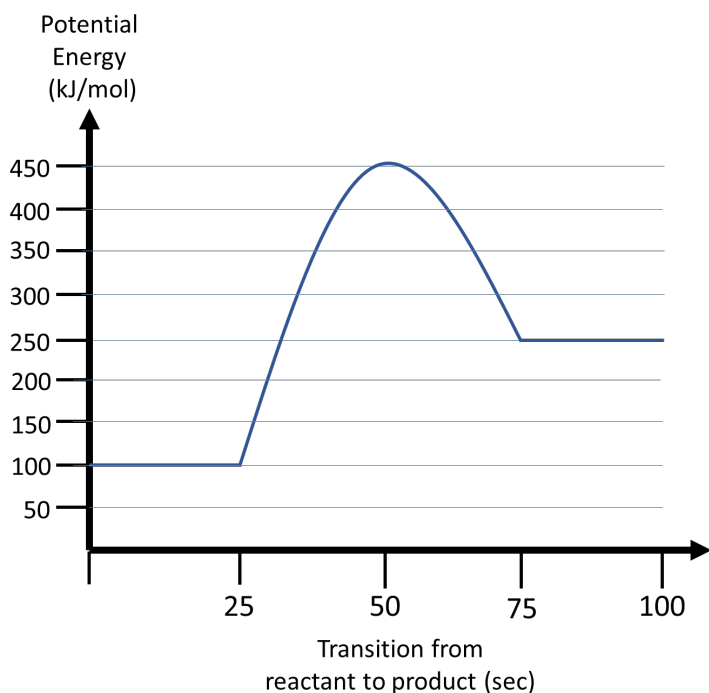
with a laser beam is  $0.03 \text{ M}^{-1} \cdot \text{sec}^{-1}$ . What is the time needed to decrease a  $5.0 \text{ mol/L}$  sample of  $\text{NO}_2$  to  $1.25 \text{ mol/L}$ ?

- (A)  $\frac{1}{2 \times 0.03} \ln\left(\frac{5.0}{1.25}\right) \text{ sec}$   
 (B)  $\frac{1}{0.03} \ln\left(\frac{5.0}{1.25}\right) \text{ sec}$   
 (C)  $\frac{1}{2 \times 0.03} \times \left(\frac{1}{1.25} - \frac{1}{5.0}\right) \text{ sec}$   
 (D)  $\frac{1}{0.03} \times \left(\frac{1}{1.25} - \frac{1}{5.0}\right) \text{ sec}$

**30.** The units of the rate constant ( $k$ ) for a reaction that occurs between two second-order reactants, using seconds as the time basis, are:

- (A)  $\text{mol}^{-1} \text{ L}^1 \text{ sec}^{-1}$   
 (B)  $\text{mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$   
 (C)  $\text{mol}^{-3} \text{ L}^3 \text{ sec}^{-1}$   
 (D)  $\text{mol}^{-4} \text{ L}^4 \text{ sec}^{-1}$

**Questions 31 and 32**  
 refer to the following energy diagram.



**31.** The graph above describes the evolution of a gaseous reaction's energy level over time. Which of the following is correct?

- (A) The reaction is exothermic and the activation energy is  $200 \text{ kJ mol}^{-1}$ .  
 (B) The reaction is exothermic and the activation energy is  $350 \text{ kJ mol}^{-1}$ .  
 (C) The reaction is endothermic and the activation energy is  $200 \text{ kJ mol}^{-1}$ .  
 (D) The reaction is endothermic and the activation energy is  $350 \text{ kJ mol}^{-1}$ .

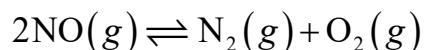
**32.** Which of the following is true concerning the effect of adding a catalyst?

- (A) The activated complex would form in less than 50 seconds.  
 (B) The energy of the reactants would be increased.  
 (C) The energy of the products would be lowered.  
 (D) More reactions would occur per second.

**33.** The Arrhenius equation can be adjusted and plotted to determine a reaction's activation energy. Letting  $k$  and  $T$  denote rate constant and temperature, respectively, which of the following combinations of variables plots as a straight line from which  $E_a$  can be established?

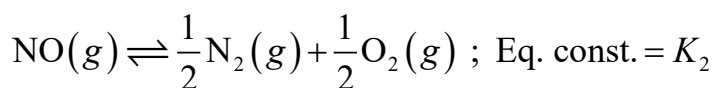
- (A)  $k$  versus  $1/T$   
 (B)  $k$  versus  $1/T^2$   
 (C)  $\ln k$  versus  $1/T$   
 (D)  $\ln k$  versus  $1/T^2$

**34.** A sample of  $\text{NO}$ ,  $\text{N}_2$  and  $\text{O}_2$  in a container undergoing the reaction below is in equilibrium. Which of the following is true?



- (A) After equilibrium is reached, the pressure of the system will gradually increase.  
 (B) After equilibrium is reached, the pressure of the system will gradually decrease.  
 (C) At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.  
 (D) At equilibrium, the rates of the forward and reverse reactions are both equal to zero.

35. Consider the following reactions.



What is the relationship between equilibrium constants  $K_1$  and  $K_2$ ?

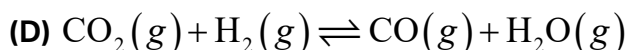
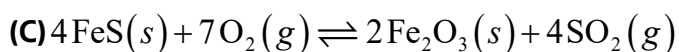
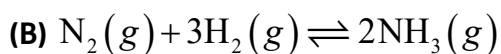
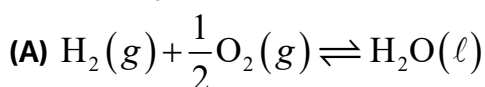
(A)  $K_1 K_2 = 1$

(B)  $K_1^2 K_2 = 1$

(C)  $K_1 K_2^2 = 1$

(D)  $K_1 = K_2^2$

36. The partial pressure-based equilibrium constant  $K_p$  equals the concentration-based equilibrium constant  $K_c$  for which of the following equilibria?



37. In which of the following circumstances is the equilibrium constant  $K_{\text{eq}}$  of a reaction always greater than 1?

(A)  $\Delta H > 0, \Delta S > 0$

(B)  $\Delta H > 0, \Delta S < 0$

(C)  $\Delta H < 0, \Delta S > 0$

(D)  $\Delta H < 0, \Delta S < 0$

38. In a Haber process, 30 moles of hydrogen gas and 30 liters of nitrogen gas were used to carry out a reaction that yielded only 50% of the expected product. What is the composition of the gaseous mixture at the end of this process?

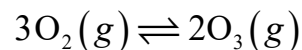
(A) 20 mol ammonia, 25 mol nitrogen gas, 15 mol hydrogen gas

(B) 10 mol ammonia, 25 mol nitrogen gas, 15 mol hydrogen gas

(C) 20 mol ammonia, 20 mol nitrogen gas, 20 mol hydrogen gas

(D) 20 mol ammonia, 10 mol nitrogen gas, 30 mol hydrogen gas

39. Stratospheric ozone is formed when oxygen interacts with a few types of radiation, in accordance with the following endothermic reaction:



Assuming Le Chatelier's principle is valid, the equilibrium can be displaced to the right (i.e., favor the formation of ozone) if we

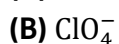
(A) Decrease temperature and decrease pressure.

(B) Decrease temperature and increase pressure.

(C) Increase temperature and decrease pressure.

(D) Increase temperature and increase pressure.

40. Which of the following **cannot** behave as both a Brønsted base and a Brønsted acid?



41. Sulfurous acid is a weak acid, while sulfuric acid is a much stronger acid. This occurs because

(A) The O—H bonds in sulfuric acid are much weaker than in sulfurous acid due to the electron withdrawing of the oxygen atoms on sulfuric acid.

(B) Sulfuric acid has more oxygen atoms in its formula.

(C) The sulfur in sulfuric acid is more electronegative than the sulfur in sulfurous acid.

(D) Sulfuric acid has the hydrogen atoms bound directly to the sulfur atom.

### Questions 42 and 43

refer to the following text and data.

In three separate experiments, a certain volume of an aqueous HCl solution was mixed with a certain volume of aqueous NaOH solution. The solutions of both reagents had the same concentration (mol/L). After mixing, an acid-base indicator was added to each of the three resulting solutions, and the following results were observed:

	Reagents	Indicator color
<b>Experiment 1</b>	2 mL HCl + 1 mL NaOH	<b>Red</b>
<b>Experiment 2</b>	2 mL HCl + 2 mL NaOH	<b>Purple</b>
<b>Experiment 3</b>	1 mL HCl + 2 mL NaOH	<b>Blue</b>

**42.** With reference to this information, which of the following is **false**?

(A) Adding the indicator used in the experiments to a solution of citric acid will turn the solution red.

(B) Adding the indicator used in the experiments to a solution of sodium chloride will turn the solution red.

(C) Adding the indicator used in the experiments to a solution of sodium acetate will turn the solution blue.

(D) Adding the indicator used in the experiments to a solution of ammonia will turn the solution blue.

**43.** Suppose the solution obtained in experiment 1 were added to the one obtained in experiment 3 and then exposed to the acid-base indicator. What would the color of the ensuing solution be?

(A) Red.

(B) Purple.

(C) Blue.

(D) There is not enough information to answer this question.

**44.** Which of the following ionic compounds will be more soluble in acid solution than in water?

(A)  $\text{BaI}_2$

(B)  $\text{PbCl}_2$

(C)  $\text{NaClO}_4$

(D)  $\text{Fe}(\text{OH})_3$

**45.** The solubility product of bismuth iodide is close to  $8 \times 10^{-19}$ . What is the molar solubility  $S$  of  $\text{BiI}_3$  in water? For the purpose of this calculation, ignore any reaction of the anion with water.

(A)  $\left(\frac{8 \times 10^{-19}}{81}\right)^{1/4}$  mol/L

(B)  $\left(\frac{8 \times 10^{-19}}{27}\right)^{1/4}$  mol/L

(C)  $\left(\frac{8 \times 10^{-19}}{81}\right)^{1/3}$  mol/L

(D)  $\left(\frac{8 \times 10^{-19}}{27}\right)^{1/3}$  mol/L

**46.** Calculate the molar solubility of  $\text{AgCl}$  in a 1.0-L solution containing 11.1 g of dissolved  $\text{CaCl}_2$ . The  $K_{sp}$  of silver chloride is  $1.6 \times 10^{-10}$ .

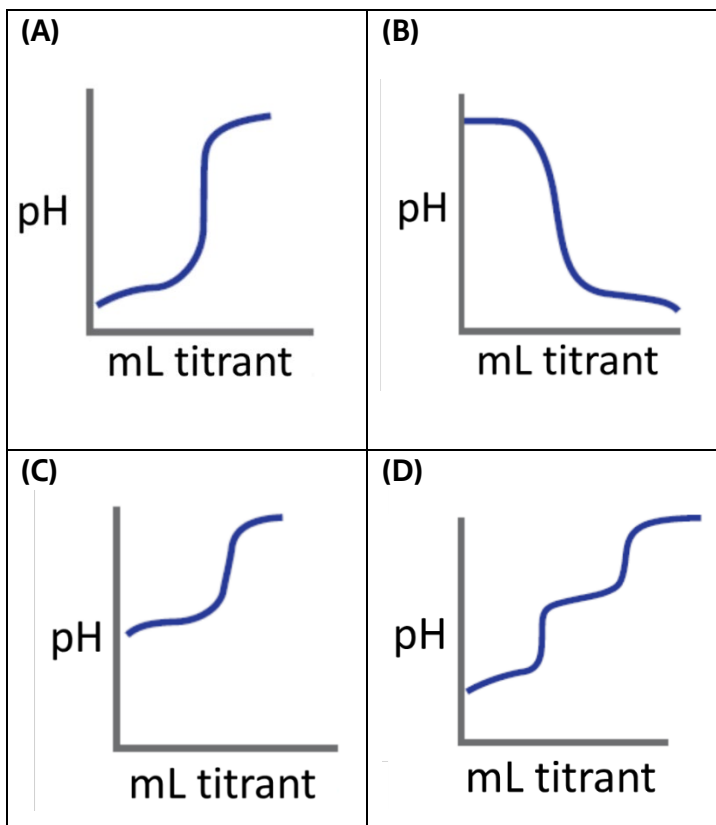
(A)  $1.6 \times 10^{-9}$  M

(B)  $3.2 \times 10^{-9}$  M

(C)  $1.6 \times 10^{-8}$  M

(D)  $3.2 \times 10^{-8}$  M

47. Which of the following titration curves could illustrate a titration process in which a strong acid is added to a strong base?



48. Which of the following is the best acid-base indicator for the detection of the end point in a titration of a weak acid and a strong base? The numbers in parentheses denote the typical pH ranges for which each indicator is applied.

- (A) Methyl orange (3 – 4)
- (B) Methyl red (5 – 6)
- (C) Bromothymol blue (6 – 7.5)
- (D) Phenolphthalein (8 – 9.6)

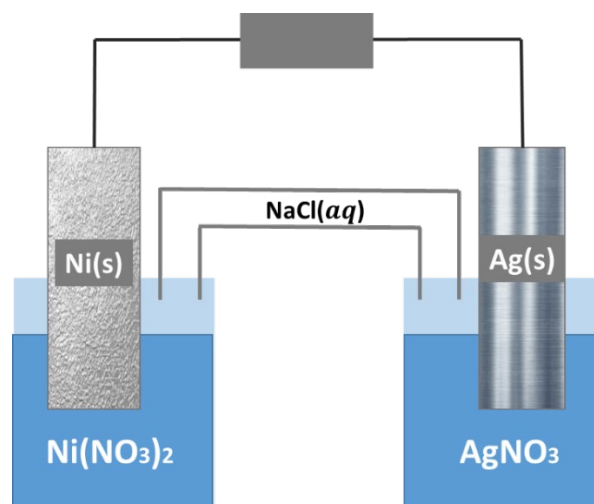
49. One liter of 1 M KCl solution is electrolyzed for 1 minute 40 sec by a current of 965 mA. Considering 100% efficiency, what will the pH of the resulting solution be?

- (A) 2
- (B) 3
- (C) 4
- (D) 5

50. Which of the following redox reactions is conventionally assigned a standard reduction potential of zero?

- (A)  $2\text{H}_2\text{O}(\ell) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$
- (B)  $\text{O}_3(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(\ell)$
- (C)  $2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$
- (D)  $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(\ell)$

Questions 51 to 54 refer to the electrochemical cell illustrated below.



Use the following standard reduction potentials whenever needed.

Reaction	$E^\circ$
$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$	-0.23 V
$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$	+0.80 V

51. Which of the following occurs at the cathode?

- (A)  $\text{Ni}^{2+}$  is reduced to  $\text{Ni}(s)$ .
- (B)  $\text{Ag}^+$  is reduced to  $\text{Ag}(s)$ .
- (C)  $\text{Ni}(s)$  is oxidized to  $\text{Ni}^{2+}$ .
- (D)  $\text{Ag}(s)$  is oxidized to  $\text{Ag}^+$

52. If the  $\text{Ni}^{2+}$  solution was replaced with a solution at a higher concentration, what would happen to the  $E^\circ$  value of the cell?

- (A) It would increase because of the presence of extra  $\text{Ni}^{2+}$  ions, which are able to donate more electrons.
- (B) It would remain the same, because  $E^\circ$  depends only on conditions in the silver half-cell.
- (C) It would decrease, because the additional  $\text{Ni}^{2+}$  ions would increase the global reaction quotient  $Q$ .
- (D) It would decrease, because the stoichiometric ratio of  $\text{Ni}^{2+}$  ions to  $\text{Ag}^+$  ions is less than 1 in the balanced global reaction.



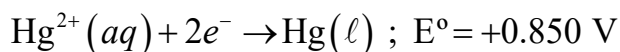
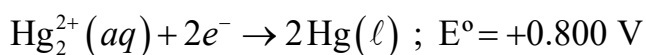
**53.** Which of the following best describes the activity in the salt bridge as the reaction progresses?

- (A) Electrons flow through the salt bridge from the Ag|Ag<sup>+</sup> half-cell to the Ni|Ni<sup>2+</sup> half-cell.
- (B) Ag<sup>+</sup> flows to the Ni|Ni<sup>2+</sup> half-cell, and Ni<sup>2+</sup> flows to the Ag|Ag<sup>+</sup> half-cell.
- (C) Na<sup>+</sup> flows to the Ag|Ag<sup>+</sup> half-cell, and Cl<sup>-</sup> flows to the Ni|Ni<sup>2+</sup> half-cell.
- (D) Na<sup>+</sup> flows to the Ni|Ni<sup>2+</sup> half-cell, and Cl<sup>-</sup> flows to the Ag|Ag<sup>+</sup> half-cell.

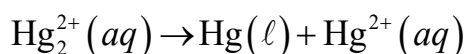
**54.** Based on the given reduction potentials, which of the following would produce the most spontaneous reaction, assuming they all occur at the same temperature?

- (A) Placing some solid nickel in a solution containing Ag<sup>+</sup> ions.
- (B) Placing some solid nickel in a solution containing Ni<sup>2+</sup> ions.
- (C) Placing some solid silver in a solution containing Ag<sup>+</sup> ions.
- (D) Placing some solid silver in a solution containing Ni<sup>2+</sup> ions.

**55.** Consider the following standard potentials at 298 K.

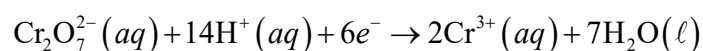


Calculate the change in Gibbs free energy for the reaction



- (A)  $-2 \times 96,500 \times 1.65 \text{ J}$
- (B)  $-2 \times 96,500 \times 0.05 \text{ J}$
- (C)  $+2 \times 96,500 \times 0.05 \text{ J}$
- (D)  $+2 \times 96,500 \times 1.65 \text{ J}$

**56.** Consider the redox reaction



What is the amount of electricity needed to produce 6 moles of Cr<sup>3+</sup> ions?

- (A)  $6 \times 96,500 \text{ C}$
- (B)  $9 \times 96,500 \text{ C}$
- (C)  $12 \times 96,500 \text{ C}$
- (D)  $18 \times 96,500 \text{ C}$

**57.** In an electrochemistry experiment, a chemistry professor filled three 50-mL beakers with 0.1 M solutions of one of three acids, HCl, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>. Afterwards, the electrical conductivity of each solution was measured, and the following results were obtained:

Solution	Conductivity (μS/cm)
I	26,000
II	9000
III	36,000

Which of the following alternatives correctly associates the solutions with the acid they contained?

	Sol. I	Sol. II	Sol. III
(A)	H <sub>3</sub> PO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>
(B)	H <sub>2</sub> SO <sub>4</sub>	HCl	H <sub>3</sub> PO <sub>4</sub>
(C)	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
(D)	HCl	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>

**58.** In order to produce fireworks of different colors, various chemical compounds are mixed to powder. When ignited with powder, some compounds made out of sodium produce yellow light, while some made out of barium lead to green light. It is known that the wavelength of yellow light is greater than that of green light. Let  $E_{\text{Na}}$  and  $E_{\text{Ba}}$  denote the energy gaps involved in emission of light by sodium and barium atoms, respectively. Further, let  $\nu_{\text{Na}}$  and  $\nu_{\text{Ba}}$  denote the velocities of the photons emitted in these processes. Which of the following is true?

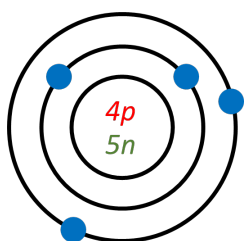
- (A)  $E_{\text{Na}} < E_{\text{Ba}}$  and  $\nu_{\text{Na}} = \nu_{\text{Ba}}$
- (B)  $E_{\text{Na}} < E_{\text{Ba}}$  and  $\nu_{\text{Na}} \neq \nu_{\text{Ba}}$
- (C)  $E_{\text{Na}} > E_{\text{Ba}}$  and  $\nu_{\text{Na}} = \nu_{\text{Ba}}$
- (D)  $E_{\text{Na}} > E_{\text{Ba}}$  and  $\nu_{\text{Na}} \neq \nu_{\text{Ba}}$

**59.** In a photochemistry experiment, a sample of bromine gas with all molecules in their neutral state is bombarded with high-energy photons; as a result, electrons are ejected from the gaseous sample. Electrons originally from which subshell would have the highest velocity after being ejected?

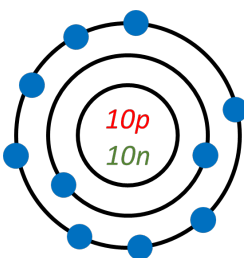
- (A)  $4s$
- (B)  $3d$
- (C)  $4p$
- (D)  $5s$

**60.** A photoelectron spectrum for which of the following atoms would show peaks at exactly three different binding energies?

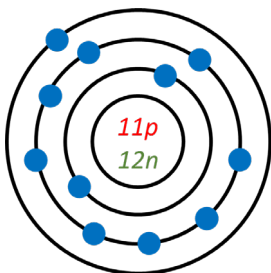
(A)



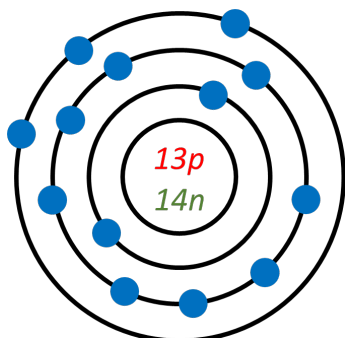
(B)



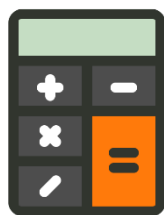
(C)



(D)



## SECTION II



**Calculators  
allowed!**

### Problem 1

A nickel(II) sulfate solution sample of unknown concentration is exposed to light in a colorimeter, and its absorbance is recorded in a Beer-Lambert law experiment. The sample is in a 1.0-cm cell and reportedly transmits 80% of light of a certain wavelength. The absorptivity at this wavelength is determined to be  $2.0 \text{ cm}^{-1} \text{ g}^{-1} \text{ L}$ .

- A.** State the relationship between absorbance and concentration, identifying all variables. (30%)
- B.** Why does a solution of nickel(II) sulfate represent a suitable solution to be studied in an experiment such as the one introduced in the problem statement, whereas a solution of potassium chloride does not? (15%)
- C.** Nickel(II) sulfate solutions are green. Why would light of a wavelength equivalent to the green part of the visible spectrum be a poor choice in the experiment in question? (15%)
- D.** Determine the concentration of the nickel(II) sulfate solution. (40%)

### Problem 2

A sample of zinc is immersed in a container filled with a solution of dilute sulfuric acid. As the metal corrodes, bubbles start to evolve from the solution.

- A.** What is the oxidation state of the zinc atoms after the metal is corroded? (15%)
- B.** Estimate the solubility of the salt formed from the corrosion of zinc by sulfuric acid, knowing that this salt has a  $K_{sp}$  of 0.36. Express your answer in g/L. (15%)
- C.** What are the bubbles of gas that evolve from the solution? Write a balanced chemical equation that explains the formation of these bubbles. (30%)
- D.** Knowing that 98.1 g of zinc were corroded in the experiment and that all gas formed in accordance with the equation you wrote in (B) was isolated, placed in a container at 298 K, and equipped with a manometer that read 0.8 atm, estimate the volume of gas obtained in the process. (40%)



### Problem 3

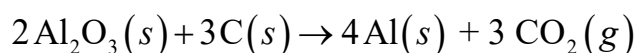
Consider the combustion of the disaccharide sucrose,  $C_{12}H_{22}O_{11}(s)$ , in an oxygen-rich atmosphere. The only products are carbon dioxide and liquid water. The pertaining standard heats of formation and molar entropies are listed below.

Compound	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$S_m^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
$C_{12}H_{22}O_{11}(s)$	-2220	360
$O_2(g)$	0	205
$CO_2(g)$	-394	214
$H_2O(l)$	-286	70

- Write a balanced equation for the combustion of sucrose. (10%)
- Calculate the standard heat of combustion for sucrose. (25%)
- How much energy is given off by the combustion of 1.0 gram of sucrose? (15%)
- Calculate the standard change in entropy for the combustion of 1 mol of glucose. (25%)
- Calculate the standard change in Gibbs free energy for the combustion of sucrose at 298 K. Is the reaction spontaneous? (25%)

### Problem 4

The refining of aluminum from bauxite ore, which can be assumed to contain 50%  $Al_2O_3$  by mass, proceeds by the electrolysis of aluminum oxide:



- In the reaction above, what is the change in oxidation number of aluminum? (10%)
- Write a chemical equation for the conversion of aqueous aluminum ion to metallic aluminum. (10%)
- In the process above, why does the anode need to be replaced regularly? (20%)
- Assuming 100% conversion, how many metric tons of bauxite ore are required to give the  $5 \times 10^{10}$  kg of aluminum produced each year in the United States? (25%)
- What is the electric current, in kA, needed for an aluminum manufacturer to produce 270 kg of the metal per day, assuming it operates 12 hours per day and the deposition process occurs with 75% efficiency? (35%)

**Problem 5**

A solution contains 0.1 M H<sub>2</sub>S and 0.3 M HCl. The first and second ionization constants of H<sub>2</sub>S are 10<sup>-7</sup> and 1.3×10<sup>-13</sup>, respectively.

- A.** An inexperienced chemistry student says that hydrogen sulfide has a linear geometry and is capable of forming hydrogen-bond intermolecular attractive forces with other H<sub>2</sub>S molecules. Are any of the student's assertions correct? Explain. (40%)
- B.** Calculate the equilibrium concentration of HS<sup>-</sup>. (30%)
- C.** Calculate the equilibrium concentration of S<sup>2-</sup>. (30%)

**Problem 6**

A 25.0-mL sample of 0.21 M dimethylamine, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH, is titrated with 0.545 M HCl. The *K<sub>b</sub>* of dimethylamine is 6.5×10<sup>-4</sup>.

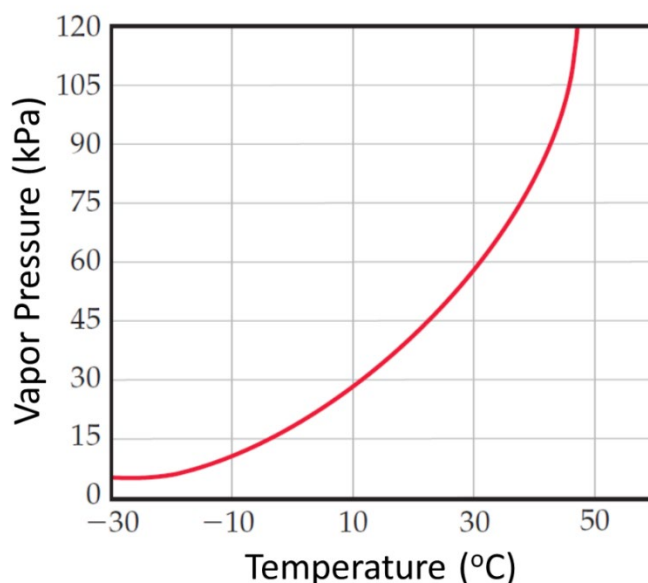
- A.** Write a balanced net ionic equation for the titration. (20%)
- B.** How many mL of HCl are required to reach the equivalence point? (25%)
- C.** Complete the following table with concentrations at the equivalence point. Assume that volumes are additive. (40%)

<i>Species</i>	<i>Concentration</i>
[(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH]	
[(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> ]	
[H <sup>+</sup> ]	
[Cl <sup>-</sup> ]	

- D.** What is the pH at the equivalence point? (15%)

**Problem 7**

The following graph shows the evolution of vapor pressure of carbon disulfide, CS<sub>2</sub>, with temperature.



**A.** Using the graph, estimate the vapor pressure of CS<sub>2</sub> at 30°C. (10%)

**B.** Using the graph, estimate the normal boiling point of CS<sub>2</sub>. (10%)

The following table gives the molecular structures and boiling points for the compounds carbon disulfide, CS<sub>2</sub>, and carbonyl sulfide, COS.

Compound	Molecular structure	Normal boiling point (°C)
CS <sub>2</sub>	S = C = S	Determined in (B)
COS	S = C = O	-50°C

**C.** In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of CS<sub>2</sub>(ℓ) is higher or lower than that of COS(ℓ). (20%)

**D.** A 20-g mass of liquid carbon disulfide is inserted in a 6.0-L rigid container. The container is sealed and heated to 350 K, at which temperature all of the CS<sub>2</sub>(ℓ) has vaporized. What is the pressure in the container since all of the CS<sub>2</sub>(ℓ) has vaporized? (20%)

The decomposition reaction of carbon disulfide, CS<sub>2</sub>, to carbon monosulfide, CS, and sulfur is first order with  $k = 3.0 \times 10^{-7} \text{ sec}^{-1}$  at 1000°C.



**E.** Determine the half-life of this reaction at 1000°C. (10%)

**F.** How many days would pass before a 20-g sample of CS<sub>2</sub> had decomposed to the extent that 7.5 g of CS<sub>2</sub> remained? (15%)

**G.** How much of a 20-g sample of CS<sub>2</sub> would remain after 60 days? (15%)



## Solutions

### → Section I

**1.B.** Neutral zinc has 30 electrons, which means that the divalent cation  $\text{Zn}^{2+}$  has 28 electrons. The nearest noble gas is argon, which has 18  $e^-$ . We are left with  $28 - 18 = 10$  electrons to distribute. Referring to an electron configuration diagram, we see that the remaining electrons can be distributed as  $4s^23d^8$ .

**2.A.** Chlorine and sulfur are in the same period and atomic size decreases across a period (increasing effective nuclear charge); thus, chlorine is smaller than sulfur. Further, atomic size increases down a main group (larger outer electron orbital) and, since selenium is right below sulfur, Se has a larger atomic size than both S and Cl.

**3.D.**  $\text{IE}_1$  decreases down a group, so tin and antimony will have smaller IEs than arsenic. (One simplistic way to explain this trend is to recall that atomic size increases as we move down a group, so the outermost electrons of a large atom such as, say, antimony will experience a milder electrostatic attraction to the nucleus than the external electrons of a smaller atom such as arsenic.) According to the “period rule,” ionization energy increases across a period, that is, as elements increase their number of protons. This implies that Sb has a higher  $\text{IE}_1$  than Sn.

**4.B.** In *P*, we have an intermolecular attractive force between a molecule’s fluorine atom, one of the three most electronegative elements, and another molecule’s hydrogen atom; this is the classic configuration for a hydrogen bond to form. In *Q*, we have an intermolecular attractive force between two diatomic, nonpolar molecules; this is the textbook setting for London dispersion forces. In *R*, a  $\text{Na}^+$  cation approaches a polar molecule, forming an ion-dipole force. Lastly, in *S* two polar molecules interact via dipole-dipole forces.

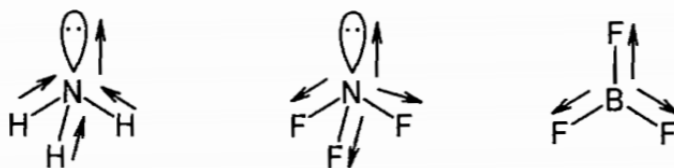
**5.B.** London dispersion forces such as the ones between fluorine gas molecules in *Q* are the weakest attractive intermolecular interactions. They are followed by dipole-dipole interactions, then by hydrogen bonds, and lastly by ion-dipole interactions.

**6.C.** The molecule would be the most stable when it has the largest attractive potential energy, which is represented by a negative sign. While the magnitude of the potential energy may be larger at (A), it is repulsive at that point because the nuclei are too close together. This leaves us with alternative C as the correct answer.

**7.D.** → A low surface tension means the attraction between molecules making up the surface is weak. Water has a high surface tension; water bugs could not “walk” on the surface of a liquid with low surface tension.  
 → A low critical temperature means a gas is very difficult to liquefy by cooling. This is the result of weak intermolecular attractions. Helium has the lowest known critical temperature ( $\approx 5.3$  K).  
 → A low boiling point means weak intermolecular interactions. It takes little energy to separate the particles. All ionic compounds have extremely high boiling points (e.g., the BP of NaCl is  $1465^\circ\text{C}$ ).  
 → A low vapor pressure means it is difficult to remove molecules from the liquid phase because of high intermolecular attractions. Substances with low vapor pressures have high boiling points.

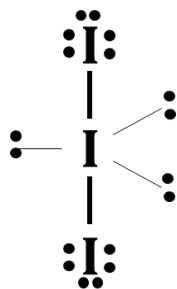
**8.B.** Statement (A) is correct, in that only methanol has an O–H bond and hence is capable of forming hydrogen bonds. Statement (C) is also correct because, when two similar compounds have intermolecular interactions by dispersion forces as in the case of Xe and Ar, the heavier compound should form the stronger dispersion forces and ultimately have the greater BP. In a similar manner, statement (D) is correct since, although both chlorine gas and krypton form dispersion forces, these are stronger in  $\text{Cl}_2$  because this compound has more electrons and is more polarizable than Kr. Statement (B) is false because acetone has no single O–H, N–H or F–H bond, which implies that it forms no hydrogen bonds. The difference in BP from acetone to 2-methylpropane is better attributed to the fact that the former is a polar molecule, which interacts with similar entities by dipole-dipole and dispersion forces. The same cannot be said of 2-methylpropane, a nonpolar molecule capable of forming only dispersion forces.

**9.B.** In the ammonia molecule, the N – H bonds that constitute the sides of the tetrahedron all have dipole moments pointing to the central nitrogen, as illustrated below; the resulting dipole is further magnified by the N atom’s lone electron pair. In the nitrogen trifluoride molecule, the fluorine atoms in the N – F bonds are more electronegative than the N atom, so the dipole moments of these bonds point *away* from the central nitrogen; this dipole orientation is counterbalanced by the N atom’s lone electron pair, but  $\text{NF}_3$  is nonetheless less polar than  $\text{NH}_3$ . Lastly, boron trifluoride has a trigonal planar structure and dipole moments in B – F bonds that ultimately cancel each other, resulting in a nonpolar molecule.



**10.D.**  $\text{I}_3^-$  is a linear ion with a total of nine lone pairs of electrons, as illustrated below.





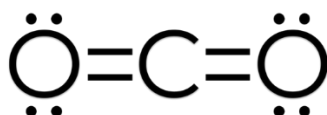
**11.C.** Water, ammonia and methane all have  $sp^3$  hybridization.

**12.D.** Carbonate, sulfur trioxide, and nitrate have central atoms with three bond pairs and no lone pairs; as a result, they have trigonal planar geometry.  $XeO_3$ , on the other hand, has one lone pair and thus exhibits a tetrahedral geometry.

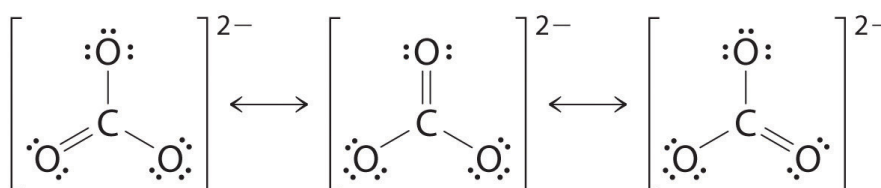
Molecule/ion	No. lone pairs + bond pairs	Geometry
$CO_3^{2-}$	0 LP + 3 BP	Trigonal planar
$SO_3$	0 LP + 3 BP	Trigonal planar
$XeO_3$	1 LP + 3 BP	Tetrahedral
$NO_3^-$	0 LP + 3 BP	Trigonal planar

**13.D.**  $CO_2$  has a bond order of 2, which exceeds the orders of the other structures. Remember that a higher bond order corresponds to shorter and stronger bonds.

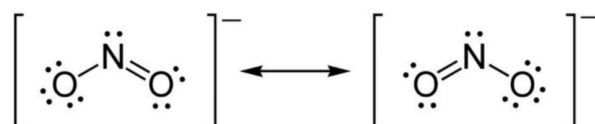
**14.D.**  $CO_2$  has a linear, non-resonant structure, as shown.



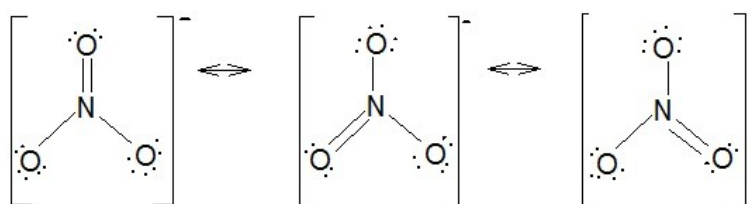
Carbonate exhibits resonance, existing in the form of three resonance structures.



Nitrite alternates between two resonance structures.



Lastly, nitrate also exists as three resonance structures.



**15.D.** Carbonate, nitrite and nitrate have three electron domains and hence display  $sp^2$  hybridization.

**16.C.** The bond angle of  $\text{NO}_2^-$  would be less than that of  $\text{NO}_3^-$  or  $\text{CO}_3^{2-}$  because the unbonded pair of electrons on the nitrogen atom reduces the overall bond angle.

**17.A.** The compressibility factor  $Z$  is defined as

$$Z = \frac{PV}{nRT}$$

For an ideal gas,  $Z = 1$  and the Clausius-Clapeyron equation holds:

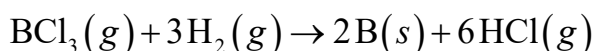
$$Z = \frac{PV}{nRT} \rightarrow PV = nRT$$

**18.B.** Upon heating, barium carbonate decomposes to BaO and  $\text{CO}_2$ ,



Thus, decomposition of one mole of  $\text{BaCO}_3$  yields one mole of  $\text{CO}_2$ . By the same token, decomposition of  $98.5/197 = 0.5$  mol of this salt releases  $0.5 \times 22.4 = 11.2$  L of carbon dioxide.

**19.C.** The reaction in question is



As can be seen, 3 moles of hydrogen are needed to produce 2 moles of boron. Since we need  $32.4/10.8 = 3$  mol of boron, the amount of gaseous hydrogen required is  $1.5 \times 3 = 4.5$  mol. Appealing to the ideal gas law, the corresponding volume of  $\text{H}_2$  is

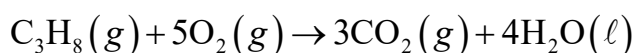
$$PV = nRT \rightarrow V = \frac{nRT}{P}$$
$$\therefore \boxed{V = \frac{4.5 \times 0.082 \times 298}{1.0} \text{ L}}$$

Carry out the calculation and you'll find 110 L.

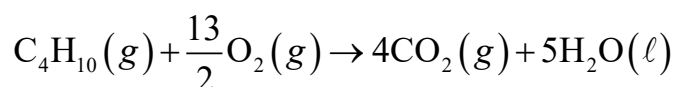
**20.B.** Let  $\alpha$  and  $\beta$  denote the volumes of  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$  in the original mixture, respectively. Initially, we have

$$\alpha + \beta = 3$$

Combustion of one mole of propane yields three moles of  $\text{CO}_2$ ,



Similarly, combustion of butane yields four moles of  $\text{CO}_2$ ,



Combining this information, we have

$$3\alpha + 4\beta = 10$$

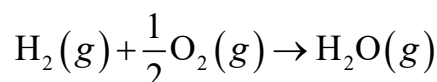
In view of the first result, we have

$$\begin{aligned}3\alpha + 4\beta = 10 &\rightarrow 3\alpha + 3\beta + \beta = 10 \\ \therefore \underbrace{3(\alpha + \beta)}_{=3} + \beta &= 10 \\ \therefore 9 + \beta &= 10 \\ \therefore \beta &= 1\text{L}\end{aligned}$$

Finally,

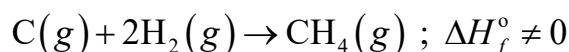
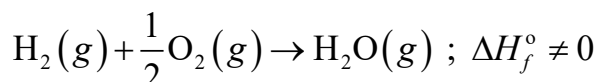
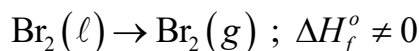
$$\begin{aligned}\alpha + \beta = 3 &\rightarrow \alpha + 1 = 3 \\ \therefore \alpha &= 2\text{L}\end{aligned}$$

**21.C.** The reaction in question is of course



We have  $2.0/2.0 = 1$  mol of hydrogen gas and  $24/32 = 0.75$  mol of oxygen. From the stoichiometry of the reaction, we see that 0.5 moles of  $\text{O}_2$  would react with 1 mole of  $\text{H}_2$  to form 1 mole of water. In proportional terms, 0.75 moles of  $\text{O}_2$  would react with 1.5 moles of  $\text{H}_2$  to yield 1.5 mol of water. However, we only have 1 mol of hydrogen gas; accordingly,  $\text{H}_2$  is a limiting reagent and only 1 mol of  $\text{H}_2\text{O}$  will be formed. This corresponds to a mass of  $1.0 \times 18 = 18$  g.

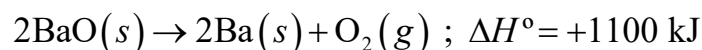
**22.B.** The standard enthalpy of formation is zero for substances made of a single element that are stable as gases at a temperature of 298 K. Bromine and chlorine gas are two potential candidates, but the former must be discarded because  $\text{Br}_2$  is a liquid at the temperature in question.



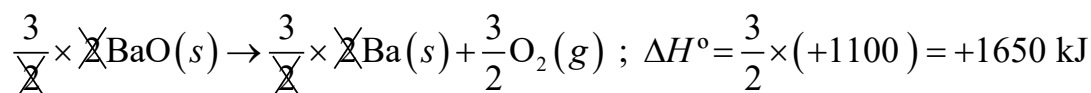
**23.A.** Fusion of a solid compound, as in the case of water in (B), is naturally accompanied by a raise in entropy. Likewise, vaporization of a compound, as in the case of fluorine in (C), occurs with a positive  $\Delta S$ . Reaction (D) begins with one equivalent of gas and ends with two equivalents of gas, so it should be accompanied by a raise in entropy. Diamond is a highly ordered structure, much more so than graphite; accordingly, the conversion of graphite to diamond would be actually followed by a *reduction* in entropy, in contrast to the other three processes.

**24.C.** A reaction taking place at 298 K will be spontaneous if its standard Gibbs free energy is lower than zero. This is the case of reaction II, but not of reaction I. Thus, reaction II is spontaneous, whereas reaction I is not.

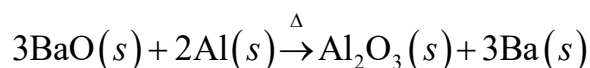
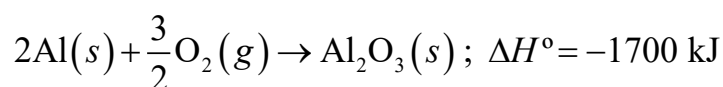
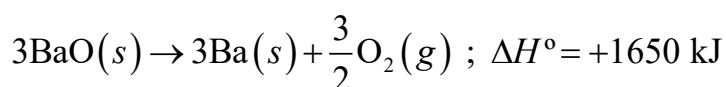
**25.B.** Notice that in the second reaction, solid aluminum is already on the side we want it to be; further, it already has a stoichiometric coefficient equal to 2. We needn't change anything on this reaction. As for the first reaction, we first perform an inversion,



Then, we multiply the stoichiometric coefficients by 3/2,



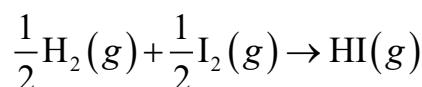
Adding the modified first equation to the second one, we get the reaction we are looking for,



which has an enthalpy such that

$$\Delta H^\circ = +1650 - 1700 = \boxed{-50 \text{ kJ}}$$

**26.C.** The pertaining reaction is the formation of hydrogen iodide from gaseous hydrogen and iodine,



which has a heat of formation equal to 27 kJ. Equipped with this enthalpy and the bond energies we were given, the bond energy we aim for easily follows,

$$27 = \frac{1}{2} \times 440 + \frac{1}{2} \times H_{I-I} - 300$$

$$\therefore 27 = 220 + \frac{1}{2} \times H_{I-I} - 300$$

$$\therefore 27 = \frac{1}{2} \times H_{I-I} - 80$$

$$\therefore H_{I-I} = 107 \times 2 = \boxed{214 \text{ kJ}}$$

**27.B.** Inspecting the table, we see that doubling the concentration of *A* while holding the concentration of *B* constant causes the reaction rate to double; thus, the exponent that accompanies [*A*] in the reaction rate law, and therefore the order of reaction with respect to *A*, should equal 1. Also from the table we see that doubling the concentration of *B* while holding the concentration of *A* constant causes the reaction rate to increase four-fold; this means that the order of reaction with respect to *B* is 2.

**28.A.** Inspecting the table, we see that it takes approximately 30 minutes to reduce the concentration of reactant by about half (i.e., from 120 to 58 g), and another 30 min or so to reduce it to a quarter of its original value (that is, from 120 to 26 g). Accordingly, the reaction is first-order in the monitored reagent and has a half-life of 28 min.

**29.C.** For the reaction  $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$ , the rate constant units,  $\text{M}^{-1} \cdot \text{sec}^{-1}$ , tell us that the reaction is second order overall. Since the reaction has only one reactant,  $\text{NO}_2$ , the reaction is second order with respect to  $\text{NO}_2$ . The integrated rate equation for a reaction that is second order with respect to  $\text{NO}_2$  as the only reactant,

$$\frac{1}{[\text{NO}_2]} - \frac{1}{[\text{NO}_2]_0} = akt$$

where  $a = 2$  is the stoichiometric coefficient of  $\text{NO}_2$ . Substituting our data brings to

$$\frac{1}{[\text{NO}_2]} - \frac{1}{[\text{NO}_2]_0} = akt \rightarrow \frac{1}{1.25} - \frac{1}{5.0} = 2 \times 0.03 \times t$$

$$\therefore t = \frac{1}{2 \times 0.03} \times \left( \frac{1}{1.25} - \frac{1}{5.0} \right) \text{sec}$$

**30.C.** Let A and B denote the reactants that determine the reaction rate. We may write

$$r = k[\text{A}]^2 [\text{B}]^2$$

If the rate  $r$  has dimensions of  $\text{M}/\text{sec}$  and the concentrations of A and B both have units of  $\text{M}$ , it follows that

$$\frac{\text{M}}{\text{sec}} = k \times \text{M}^2 \times \text{M}^2$$

$$\therefore \frac{\text{M}}{\text{sec}} = k \times \text{M}^4$$

$$\therefore k = \frac{\text{M}^{-3}}{\text{sec}}$$

$$\therefore k = \frac{(\text{mol L}^{-1})^{-3}}{\text{sec}}$$

$$\therefore k = \boxed{\text{mol}^{-3} \text{L}^3 \text{sec}^{-1}}$$

**31.D.** Since the energy level of the products is greater than that of the reactants, the reaction is endothermic. (The heat of reaction is easily seen to be  $250 - 100 = 150 \text{ kJ mol}^{-1}$ .) The activation energy is the difference between the highest energy level achieved in the transition from reactants to products, which is seen to be  $450 \text{ kJ mol}^{-1}$ , and the starting energy level

of the reactants, which is  $100 \text{ kJ mol}^{-1}$ ; thus,  $E_a = 450 - 100 = 350 \text{ kJ mol}^{-1}$ .

**32.D.** Addition of a catalyst would increase the rate at which effective collisions occur, and more reactions would occur per second. The catalyst would not affect the energy level of reactants or products, nor would it speed up the formation of the activated complex.

**33.C.** Per the Arrhenius equation, the rate constant is related to the activation energy by an expression of the form

$$k = Ae^{-E_a/RT}$$

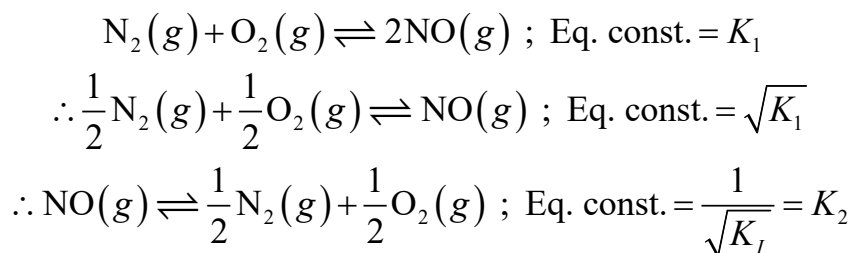
Taking logarithms on both sides and manipulating, we get

$$\begin{aligned}\ln k &= \ln(Ae^{-E_a/RT}) \\ \therefore \ln k &= \ln A + \ln e^{-E_a/RT} \\ \therefore \ln k &= \ln A - \frac{E_a}{RT} \\ \therefore \ln k &= -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A\end{aligned}$$

Thus, a plot of  $\ln k$  versus reciprocal temperature is a straight line whose slope can be used to establish the value of activation energy  $E_a$ .

**34.C.** At equilibrium, the partial pressures of each gas remain the same and the pressure of the system remains unchanged. The forward and reverse reactions continue to occur, but they do so at the same rate; as a result, the composition of the system is unaltered.

**35.C.** Taking the first reaction as a reference, we have



That is,

$$\frac{1}{\sqrt{K_1}} = K_2 \rightarrow \boxed{K_1 K_2^2 = 1}$$

**36.D.** Noting that  $K_p = K_c(RT)^{\Delta n}$ , the two equilibrium constants will have the same value if  $\Delta n = 0$ , that is, if the number of equivalents of gas is the same on both sides of the reaction. Such is the case of reaction (C), where we have two equivalents of gas on the side of the reactants and two equivalents of gas on the side of the products.

**37.C.** Recall that  $\Delta G = -RT \ln K_{eq}$ , so  $K_{eq} = \exp(-\Delta G/RT)$ . Clearly, the lower (more negative)  $\Delta G$  is, the more the forward reaction will be favored and the greater  $K_{eq}$  will be. Knowing that  $\Delta G = \Delta H - T\Delta S$ , a reaction with negative  $\Delta H$  (exothermic) and positive  $\Delta S$  (increase in entropy) should lead to  $K_{eq} > 1$ .

**38.B.** Normally, 30 moles of nitrogen would react with 90 moles of hydrogen to yield 60 moles of ammonia:

$N_2(g)$	$3 H_2(g)$	→	$2 NH_3(g)$
30 mol	90 mol		60 mol

However, we only have 30 moles of hydrogen gas, so  $H_2$  acts as a limiting reagent.

$N_2(g)$	$3 H_2(g)$	→	$2 NH_3(g)$
10 mol	30 mol		20 mol

We were told that the reaction yielded only 50% of the expected product, so only 5 mol of  $N_2$  and 15 mol  $H_2$  reacted, and only 10 mol of ammonia were produced.

$N_2(g)$	$3 H_2(g)$	→	$2 NH_3(g)$
5 mol	15 mol		10 mol

Lastly, the final mixture should contain 10 moles of ammonia,  $30 - 5 = 25$  mol of  $N_2$ , and  $30 - 15 = 15$  mol of  $H_2$ .

**39.D.** Increasing temperature will favor the endothermic reaction – in this case, the formation of ozone. Increasing pressure will favor the reaction with less equivalents of gas – again, the formation of ozone.

**40.B.** Monohydrogen phosphate ion can donate a proton to form phosphate ( $PO_4^{3-}$ ) or receive a proton to form dihydrogen phosphate ( $H_2PO_4^-$ ). Bicarbonate ion ( $HCO_3^-$ ) can donate a proton to form carbonate ( $CO_3^{2-}$ ) or receive one to form carbonic acid ( $H_2CO_3$ , which rapidly dissociates to carbon dioxide and water in most settings of chemical interest). Hydrogen sulfate/bisulfate ( $HSO_4^-$ ) can donate a proton to form sulfate ( $SO_4^{2-}$ ) or receive one to form sulfuric acid ( $H_2SO_4$ ). Perchlorate ion ( $ClO_4^-$ ) can receive a proton to form perchloric acid ( $HClO_4$ ), but it has no hydrogen atom to give away; accordingly,  $ClO_4^-$  can function as a Brønsted base, but not as an acid.

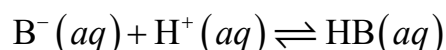
**41.A.** Weak O–H bonds make for stronger acids.

**42.B.** Statement (A) is correct because citric acid is, wait for it, an acid, and experiment 1 shows that the indicator will turn red in the presence of excess acid. Statement (C) is correct because sodium acetate derives from a strong base (NaOH) and should turn the solution blue; experiment 3 shows that the indicator will exhibit this color when placed in an alkaline medium. The same applies when the indicator is exposed to ammonia, a

base, so statement (D) is correct. It remains to evaluate statement (B); sodium chloride, NaCl, derives from a strong base (NaOH) and a strong acid (HCl), so it should favor neither the formation of hydronium nor the formation of hydroxyl ions by salt hydrolysis. Thus, a solution of NaCl when exposed to the indicator in question should remain purple, which is the color the indicator displays when exposed to a solution of neutral pH.

**43.B.** Experiment 1 has 2 mL of solution of HCl, a monoprotic acid, and 2 mL of solution of NaOH, a monobasic base. Experiment 3 has 1 mL of HCl solution and 2 mL of NaOH solution. Adding experiment 1 to experiment 3 produces a solution with 2 + 1 mL of HCl solution and 1 + 2 mL of NaOH solution. Since the concentrations of the starting acid and base solution concentrations are the same, and assuming complete dissociation, the 3 mL of acid solution will exactly neutralize the 3 mL of base solution. The final mixture will have neutral pH and be purple in color.

**44.D.** When the anion of a salt is a base, the salt will be more soluble in acidic solution because the hydrogen ion decreases the concentration of the anion (Le Chatelier's principle):



The solubility of  $\text{BaI}_2$  in acid is unchanged over the solubility in pure water because hydroiodic acid, HI, is a strong acid, and therefore  $\text{I}^{-}$  is a negligibly weak base. A similar reasoning applies to  $\text{PbCl}_2$  and  $\text{NaClO}_4$ , whose anions are weak bases because they derive from the strong acids HCl and  $\text{HClO}_4$ . Iron(III) hydroxide is derived from water, a weak acid, which implies that hydroxyl is a moderate-to-strong base.

**45.B.** First, we draw up a concentration table.

	$\text{BiI}_3(\text{s})$	$\leftrightarrow$	$\text{Bi}^{3+}(\text{aq})$	$3\text{I}^{-}(\text{aq})$
Initial composition	–	$\leftrightarrow$	0	0
Change in comp.	–	$\leftrightarrow$	$S$	$3S$
Final comp.	–	$\leftrightarrow$	$S$	$3S$

From the law of mass action, we have

$$K_{sp} = [\text{Bi}^{3+}][\text{I}^{-}]^3 \rightarrow 8 \times 10^{-19} = (S) \times (3S)^3$$

$$\therefore 8 \times 10^{-19} = 27S^4$$

$$\therefore S = \left( \frac{8 \times 10^{-19}}{27} \right)^{1/4} \text{ mol/L}$$

**46.A.** The molar mass of  $\text{CaCl}_2$  is  $40 + 2 \times 35.5 = 111$  g/mol, and the molarity of the starting solution is



$$m = \frac{11.1 \text{ g CaCl}_2}{111 \text{ g CaCl}_2} \times 1.0 \text{ L} = 0.1 \text{ M CaCl}_2$$

mol

Letting  $s$  denote the concentration change in silver chloride, we have

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

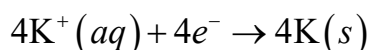
$$\therefore K_{sp} = s \times \underbrace{(0.1 - s)}_{\approx 0.1} = 1.6 \times 10^{-10}$$

$$\therefore s = \frac{1.6 \times 10^{-10}}{0.1} = \boxed{1.6 \times 10^{-9} \text{ M}}$$

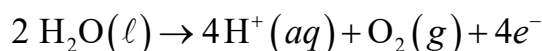
**47.B.** Titrating a strongly basic solution with a strong acid would imply beginning with a relatively high pH and then decreasing it as the acid is administered; the only curve that displays such a behavior is the one in option (B). Option (A) could be a titration in which a strong base is added to a strong acid. Option (C) could be a titration in which a strong base is added to a weak acid. Option (D) could be a titration in which a strong base is added to a polyprotic acid.

**48.B.** The pH of a solution of weak acid with a strong base should have a high pH, so the acid-base indicator used should be able to change color at a pH range substantially greater than 7. Phenolphthalein works at  $\text{pH} \in (8, 9.6)$  and hence seems to be a good candidate.

**49.D.** The redox reactions are, at the cathode,



and, at the anode,



Clearly, reduction of one equivalent of potassium ion produces one equivalent of protons. The electrical charge involved in the process is  $0.965 \text{ A} \times 100 \text{ sec} = 96.5 \text{ C}$ . Thus,

$$\frac{96,500 \text{ C}}{1 \text{ mol H}^+} = \frac{96.5 \text{ C}}{n}$$

$$\therefore n = 10^{-3} \text{ mol H}^+$$

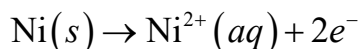
The volume of the solution is 1 L, so  $[\text{H}^+] = 10^{-3}/1.0 = 10^{-3} \text{ M}$ . Lastly, the pH is

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} 10^{-3} = \boxed{3}$$

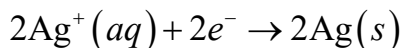
**50.C.** The reduction of  $\text{H}^+$  to hydrogen gas is conventionally assigned a reduction potential of zero; this is the so-called *standard hydrogen electrode*. Reaction (A) has  $E^\circ = -0.83 \text{ V}$  relatively to the SHE; reaction (B) has  $E^\circ = +2.07 \text{ V}$ ; reaction (D) has  $E^\circ = +1.23 \text{ V}$ .

**51.B.** The cathode is the half-cell in which reduction occurs.  $\text{Ag}^+|\text{Ag}(s)$  has a greater reduction potential than  $\text{Ni}^{2+}|\text{Ni}(s)$ , so silver ions will take up electrons and undergo deposition in the solid silver electrode.

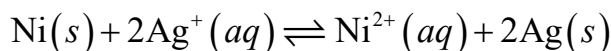
**52.C.** The anodic semireaction is



The cathodic semireaction is



Adding the two reactions brings to



The reaction quotient is then

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

Referring to the Nernst equation, we have

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

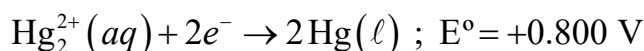
$$\therefore E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

Clearly, increasing the concentration of nickel(II) ions would raise the reaction quotient  $Q$  and increase the magnitude of the second term on the right-hand side, diminishing the reaction potential  $E$  relatively to its standard value  $E^{\circ}$ .

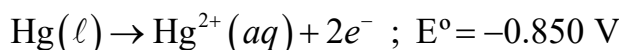
**53.C.** As the reaction progresses,  $\text{Ag}^{+}$  is being reduced to yield solid silver; this loss of positive ions is continuously counterbalanced by migration of  $\text{Na}^{+}$  to the  $\text{Ag}|\text{Ag}^{+}$  half-cell via the salt bridge. In a similar manner, increase in concentration of  $\text{Ni}^{2+}$  as the nickel electrode is corroded is counterbalanced by movement of chloride anions towards that section of the cell.

**54.A.** Reaction (A) would have a  $E^{\circ} = +0.23 + 0.80 = 1.03$  V. Reaction (B) would have a  $E^{\circ} = +0.23$  V. Reaction (C) would have a  $E^{\circ} = -0.80$  V. Reaction (D) would have a  $E^{\circ} = -1.03$  V. Since  $\Delta G^{\circ} = -nFE^{\circ}$ , the greater (more positive) potential a reaction has, the more negative  $\Delta G^{\circ}$  will be and, accordingly, the more spontaneous the reaction will turn out. Reaction (A) should be the most spontaneous one.

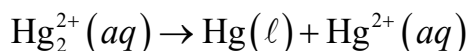
**55.C.** We take the first reaction as it is,



and reverse the second,



Adding the two equations brings to the reaction



which has a standard potential  $E^\circ = +0.800 - 0.850 = -0.05$  V. The change in Gibbs free energy is then

$$\Delta G^\circ = -nFE^\circ = -2 \times 96,500 \times (-0.05) = \boxed{+2 \times 96,500 \times 0.05 \text{ J}}$$

**56.D.** From the stoichiometry of the reaction, we see that 6 moles of electrons produce 2 moles of  $\text{Cr}^{3+}$ ; thus, in order to produce 6 moles of  $\text{Cr}^{3+}$  we'd need  $6 \times 3 = 18$  moles of electrons, which corresponds to a charge of  $18 \times 96,500 = 1.74 \times 10^6$  C.

**57.D.** The conductivity of a solution is proportional to its concentration of electrolytes.  $\text{H}_3\text{PO}_4$  is the only weak acid, which means that will only mildly dissociate in solution; as a result, we can surmise that solution II, which has the lowest conductivity of the three samples, most likely contained phosphoric acid. In turn, HCl and  $\text{H}_2\text{SO}_4$  are both strong acids, but sulfuric acid is diprotic and should dissociate into a greater amount of ions when placed in solution; accordingly, solution I likely contained HCl, while solution III contained  $\text{H}_2\text{SO}_4$ .

**58.A.** First, it goes without saying that photons of yellow or green light will both propagate with the same velocity, namely the speed of light in the lower atmosphere; this excludes alternatives (B) and (D). The energy of a photon is given by  $E = hf$ , where  $h$  is Planck's constant and  $f$  is the light's frequency. Noting that  $c = \lambda f$  or  $f = c/\lambda$ , we have

$$E = hf \rightarrow E = \frac{hc}{\lambda}$$

Since the wavelength of light emitted by stimulation of sodium atoms is greater than  $\lambda$  of light emitted by stimulation of barium atoms, it follows that  $E_{\text{Na}} < E_{\text{Ba}}$ .

**59.C.** The farther away an electron is from the nucleus, the weaker its attraction to the nucleus is and the easier it is to strip it from the atomic orbit. Upon absorbing energy from photons, electrons positioned far from the nucleus also have a greater share of energy to convert to kinetic energy. Bromine has an electronic configuration  $[\text{Ar}]4s^23d^{10}4p^5$ , so electrons from the  $4p$  subshell are certain to have the highest kinetic energy when Br atoms are bombarded with high-energy photons.

**60.B.** Diagram B represents an atom of neon, which has three subshells:  $1s$ ,  $2s$ , and  $2p$ . Electrons from each subshell would have a different binding energy, yielding three peaks on a PES.



## Answer Summary

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

### → Section II

#### Problem 1

(A) The absorbance  $A$  of a solution in a colorimeter is related to the concentration  $c$  by an expression of the form

$$A = abc$$

where  $a$  is absorptivity (or molar absorptivity, when measured in terms of molar concentration) and  $b$  is the pathlength.

(B) A solution of nickel(II) sulfate is green, but a solution of potassium chloride is colorless. As such, potassium chloride solutions do not vary in absorbance as a function of concentration.

(C) Green solutions reflect green light and will not absorb light with a wavelength in the green part of the visible spectrum. In experiments such as this, one should use radiation with a wavelength that causes the maximum absorbance, i.e., the opposite of green light, which is red light.

(D) The absorbance  $A$  is related to the transmittance  $T$  by an expression of the form

$$A = \log_{10} \frac{1}{T} = \log_{10} \frac{1}{0.8} = 0.0969$$

Then, substituting  $a = 2.0 \text{ cm}^{-1}\text{g}^{-1}\text{L}$  and  $b = 1.0 \text{ cm}$  into the Beer-Lambert law gives

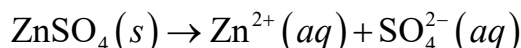
$$A = abc \rightarrow 0.0969 = 2.0 \times 1.0 \times c$$

$$\therefore \boxed{c = 0.048 \text{ g/L}}$$

### Problem 2

(A) As metallic zinc is corroded by sulfuric acid, zinc sulfate,  $\text{ZnSO}_4$ , is formed. The oxidation state of zinc in this ionic compound is +2.

(B) Zinc sulfate dissociates into  $\text{Zn}^{2+}(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$  in accordance with the reaction



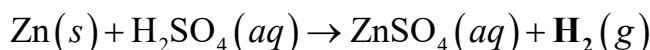
Appealing to the law of mass action, we have

$$K_{sp} = [\text{Zn}^{2+}][\text{SO}_4^{2-}] \rightarrow 0.36 = S \times S$$

$$\therefore S = \sqrt{0.36} = 0.6 \text{ mol/L}$$

$$\therefore S = 0.6 \frac{\text{mol}}{\text{L}} \times 161 \frac{\text{g}}{\text{mol}} = \boxed{96.6 \text{ g/L}}$$

(C) The bubbles formed as zinc is corroded by  $\text{H}_2\text{SO}_4$  are gaseous hydrogen, formed as a byproduct of the corrosion of metallic zinc by  $\text{H}_2\text{SO}_4$ .



(D) Inspecting the chemical reaction shown in the previous part, it is easy to see that corrosion of 1 mole, or 65.4 g, of metallic zinc will lead to the production of 1 mole of gaseous hydrogen. Thus, if  $n$  moles of  $\text{H}_2$  are produced by the corrosion of 98.1 g of Zn, we may write

$$\frac{65.4 \text{ g Zn}}{1 \text{ mol H}_2} = \frac{98.1 \text{ g Zn}}{n}$$

$$\therefore n = \frac{98.1}{65.4} = 1.5 \text{ mol H}_2$$

The volume of gas is given by the ideal gas law,

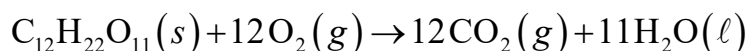
$$PV = nRT \rightarrow V = \frac{nRT}{P}$$

$$\therefore V = \frac{1.5 \times 0.0821 \times 298}{0.8} = \boxed{45.9 \text{ L}}$$

About 46 liters of  $\text{H}_2$  will have been isolated in the process.

### Problem 3

(A) Balancing combustion equations is an elementary task and should be effortless for AP Chemistry test-takers.



(B) The heat of combustion for sucrose is given by

$$\begin{aligned} \Delta H^\circ &= 12\Delta H_f^\circ[\text{CO}_2(g)] + 11\Delta H_f^\circ[\text{H}_2\text{O}(\ell)] \\ &\quad - 12\Delta H_f^\circ[\text{O}_2(g)] - \Delta H_f^\circ[\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)] \end{aligned}$$

$$\therefore \Delta H^\circ = 12 \times (-394) + 11 \times (-286) - 12 \times 0 - (-2220) = \boxed{-5650 \text{ kJ}}$$

(C) One gram of sucrose contains  $1/342 = 0.00292$  mol of this substance. Given  $\Delta H^\circ = -5650$  kJ, the amount of heat  $Q$  released by oxidation of the amount of glucose in question is

$$Q = 0.00292 \times 5650 = \boxed{16.5 \text{ kJ}}$$

(D) The change in entropy for combustion of 1 mol of glucose is

$$\begin{aligned} \Delta S^\circ &= 12S_m^\circ[\text{CO}_2(g)] + 11S_m^\circ[\text{H}_2\text{O}(\ell)] \\ &\quad - 12S_m^\circ[\text{O}_2(g)] - S_m^\circ[\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)] \end{aligned}$$

$$\therefore \Delta S^\circ = 12 \times 214 + 11 \times 70 - 12 \times 205 - 360 = \boxed{518 \text{ JK}^{-1}}$$

(E) Given the results of parts (B) and (D), all we have to do is apply the formula

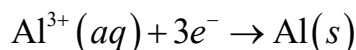
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -5650 - 298 \times 0.518 = \boxed{-5800 \text{ kJ}}$$

Since  $\Delta G^\circ$  is well below zero, we surmise that the oxidation of sucrose at 298 K is a spontaneous reaction.

#### Problem 4

(A) The aluminum in  $\text{Al}_2\text{O}_3$  changes from an oxidation state of +3 to zero; since it is reduced, it is the *oxidizing agent*. The solid carbon atoms in the reactants' side is incorporated in carbon dioxide and changes its oxidation state from zero to +4; since it is oxidized, it is the *reducing agent*. AP Topic 4.7 says the meaning of the terms "reducing agent" and "oxidizing agent" is not covered in the exam.

(B) The reduction of aluminum cations should be familiar to most students:



(C) The carbon/graphite anode reacts with oxygen to form carbon dioxide gas. Thus, the anodic graphite must be replaced from time to time.

(D) Inspecting the chemical equation we were given, we see that 2 moles of aluminum oxide are required to produce 4 moles of metallic aluminum. Accordingly, to produce  $(5 \times 10^{13})/27$  mol of aluminum we require

$$\begin{aligned} \frac{2 \text{ mol Al}_2\text{O}_3}{4 \text{ mol Al}} &= \frac{n}{(5 \times 10^{13})/27 \text{ mol Al}} \\ \therefore n &= \frac{(5 \times 10^{13})}{2 \times 27} = 9.26 \times 10^{11} \text{ mol Al}_2\text{O}_3 \end{aligned}$$

or, in terms of mass,

$$m = 9.26 \times 10^{11} \text{ mol Al}_2\text{O}_3 \times \frac{102 \text{ g Al}_2\text{O}_3}{1 \text{ mol Al}_2\text{O}_3} = 9.45 \times 10^{13} \text{ g Al}_2\text{O}_3$$

Lastly, since 1 kg of bauxite should contain 0.5 kg of  $\text{Al}_2\text{O}_3$ ,

$$\frac{0.5 \text{ kg Al}_2\text{O}_3}{1 \text{ kg Bauxite}} = \frac{9.45 \times 10^{10} \text{ kg Al}_2\text{O}_3}{m}$$

$$\therefore m = 1.89 \times 10^{11} \text{ kg Bauxite}$$

$$\therefore \boxed{m = 1.89 \times 10^8 \text{ t Bauxite}}$$

**(E)** As shown in part (B), to produce one kmol, or 27 kg, of metallic aluminum we need 3 kmol of electrons. To produce 270 kg of the metal, then, we'd require 30 kmol of electrons, which amounts to a charge of  $30,000 \times 96,500 = 2.90 \times 10^9 \text{ C}$ . Since the process operates at 75% efficiency, we'd have to increase this amount by a factor of  $1/0.75$ , giving

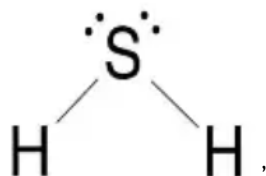
$$q = \frac{2.90 \times 10^9 \text{ C}}{0.75} = 3.87 \times 10^9 \text{ C}$$

The aluminum manufacturer operates 12 hours per day, or  $12 \times 3600 = 4.32 \times 10^4 \text{ sec}$  per day. The current we aim for is therefore

$$i = \frac{q}{\Delta t} = \frac{3.87 \times 10^9}{4.32 \times 10^4} = 89,600 \text{ A} = \boxed{89.6 \text{ kA}}$$

### Problem 5

**(A)** Hydrogen sulfide is not linear because, in addition to the two S–H bonds, the sulfur atom has two lone pairs of electrons that repel these two bonds. The result is a bent molecule, as illustrated below.



The suggestion that hydrogen sulfide molecules form hydrogen bonds with each other is also false, because in order to generate such intermolecular interactions the molecule must have a H atom linked to one of the three most electronegative elements, namely F, O, or N.

**(B)** The first dissociation of  $\text{H}_2\text{S}$  is described by the reaction

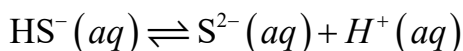


Due to the common ion effect, the concentration of  $\text{H}^+$  comes from the dissociation of HCl. Appealing to the law of mass action, we have

$$K_{a,1} = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]} \rightarrow 10^{-7} = \frac{[\text{HS}^-] \times 0.3}{0.1}$$

$$\therefore [\text{HS}^-] = \frac{0.1 \times 10^{-7}}{0.3} = \boxed{3.33 \times 10^{-8} \text{ M}}$$

**(C)** The second dissociation of  $\text{H}_2\text{S}$  is described by the reaction



so that

$$K_{a,2} = \frac{[\text{H}^{+}][\text{S}^{2-}]}{[\text{HS}^{-}]}$$

Multiplying  $K_{a,1}$  by  $K_{a,2}$  brings to

$$K_{a,1} \times K_{a,2} = \frac{\cancel{[\text{HS}^{-}]}[\text{H}^{+}]}{[\text{H}_2\text{S}]} \times \frac{[\text{H}^{+}][\text{S}^{2-}]}{\cancel{[\text{HS}^{-}]}}$$

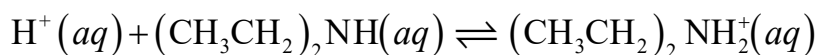
$$\therefore K_{a,1} \times K_{a,2} = \frac{[\text{H}^{+}]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$\therefore 10^{-7} \times (1.3 \times 10^{-13}) = \frac{0.3^2 \times [\text{S}^{2-}]}{0.1}$$

$$[\text{S}^{2-}] = \frac{10^{-7} \times (1.3 \times 10^{-13})}{0.3^2} \times 0.1 = \boxed{1.44 \times 10^{-20} \text{ M}}$$

### Problem 6

(A) The net ionic equation is shown below.



(B) The volume  $V$  of HCl required to reach the equivalence point is

$$V = 25.0 \text{ mL } (\text{CH}_3\text{CH}_2)_2\text{NH} \times \frac{0.21 \text{ mmol } (\text{CH}_3\text{CH}_2)_2\text{NH}}{1 \text{ mL sol.}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol } (\text{CH}_3\text{CH}_2)_2\text{NH}} \\ \times \frac{1 \text{ mL HCl}}{0.545 \text{ mmol HCl}} = \boxed{9.63 \text{ mL HCl}}$$

(C) At the equivalence point, there is no excess acid or base, only salt and water. The pH of the salt solution,  $(\text{CH}_3\text{CH}_2)_2\text{NH}_2^{+}\text{Cl}^{-}$ , is lower than 7 because we have the salt of a weak base and a strong acid. The concentration of dimethylammonium ion,  $(\text{CH}_3\text{CH}_2)_2\text{NH}_2^{+}$ , determines the pH of the system. With this in mind, we compute the amount of HCl and  $(\text{CH}_3\text{CH}_2)_2\text{NH}$  involved in the titration,

$$\begin{aligned} ? \text{ mmol HCl} &= \text{mmol } (\text{CH}_3\text{CH}_2)_2\text{NH} = \frac{0.21 \text{ mmol } (\text{CH}_3\text{CH}_2)_2\text{NH}}{\text{mL}} \times 25 \text{ mL} \\ &= 5.25 \text{ mmol } (\text{CH}_3\text{CH}_2)_2\text{NH} \end{aligned}$$

Then, we prepare the following equilibrium table:

	HCl	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	$\rightarrow$	$(\text{CH}_3\text{CH}_2)_2\text{NH}_2^{+}$
Initial composition	5.25	5.25	$\rightarrow$	0
Change in comp.	-5.25	-5.25	$\rightarrow$	+5.25
Final comp.	0	0	$\rightarrow$	5.25

The concentration of dimethylammonium ion is then



$$\left[ (\text{CH}_3\text{CH}_2)_2\text{NH}_2^+ \right] = \frac{5.25 \text{ mmol}}{25 \text{ mL} + 9.63 \text{ mL}} = 0.152 \text{ M}$$

Let  $x$  denote the concentration of hydrolyzed  $(\text{CH}_3\text{CH}_2)_2\text{NH}_2^+$ . It follows that

$$\left[ (\text{CH}_3\text{CH}_2)_2\text{NH}_2^+ \right] = 0.152 - x$$

$$\left[ (\text{CH}_3\text{CH}_2)_2\text{NH} \right] = \left[ \text{H}_3\text{O}^+ \right] = x$$

and

$$K_a = \frac{K_w}{K_{b((\text{CH}_3\text{CH}_2)_2\text{NH})}} = \frac{10^{-14}}{6.5 \times 10^{-4}} = 1.54 \times 10^{-11} = \frac{\left[ (\text{CH}_3\text{CH}_2)_2\text{NH} \right] \left[ \text{H}_3\text{O}^+ \right]}{\left[ (\text{CH}_3\text{CH}_2)_2\text{NH}_2^+ \right]}$$

$$\therefore 1.54 \times 10^{-11} = \frac{x \times x}{0.152 - x} = \frac{x^2}{0.152 - x}$$

With  $0.152 - x \approx 0.152$ , it follows that

$$1.54 \times 10^{-11} \approx \frac{x^2}{0.152}$$

$$\therefore x = \sqrt{0.152 \times (1.54 \times 10^{-11})} = 1.53 \times 10^{-6} \text{ M}$$

The following table summarizes the concentrations determined.

Species	Concentration
$\left[ (\text{CH}_3\text{CH}_2)_2\text{NH} \right]$	$1.53 \times 10^{-6} \text{ M}$
$\left[ (\text{CH}_3\text{CH}_2)_2\text{NH}_2^+ \right]$	$0.152 \text{ M}$
$\left[ \text{H}^+ \right]$	$1.53 \times 10^{-6} \text{ M}$
$\left[ \text{Cl}^- \right]$	$0.152 \text{ M}$

**(D)** It remains to establish the pH at the equivalence point,

$$\text{pH} = -\log_{10} (1.53 \times 10^{-6}) = \boxed{5.82}$$

### Problem 7

**(A)** By inspection, we see that the vapor pressure of  $\text{CS}_2$  at  $30^\circ\text{C}$  is close to 60 kPa.

**(B)** The normal boiling point is the temperature at which the vapor pressure is equal to the standard sea-level atmospheric pressure, which is  $101,325 \text{ Pa} \approx 100 \text{ kPa}$ . Draw a horizontal line at the ordinate 100 kPa (i.e., quite close to 105 kPa) and extend it until it reaches the red curve; then, project it downwards and read the corresponding temperature. In doing so, we should find a BP close to  $47.5^\circ\text{C}$ .

**(C)**  $\text{CS}_2$  has only London dispersion forces, while  $\text{COS}$  has London dispersion forces and dipole-dipole forces. The London dispersion forces in  $\text{CS}_2$  are stronger than the combination of London dispersion forces and dipole-dipole forces in  $\text{COS}$ .

**(D)** The molar mass of  $\text{CS}_2$  is  $12 + 2 \times 32 = 76 \text{ g/mol}$ , so a sample of 20 g of  $\text{CS}_2$  amounts to  $20/76 = 0.263 \text{ mol}$ . The pressure in the container follows from the ideal gas law,

$$PV = nRT \rightarrow P = \frac{nRT}{V}$$

$$\therefore P = \frac{0.263 \times 0.0821 \times 350}{6.0} = \boxed{1.26 \text{ atm}}$$

(E) The half-life of a first-order reaction is simply

$$t_{1/2} = \frac{\ln 2}{ak}$$

where  $\ln 2 = 0.693$ ,  $a = 1$  is the stoichiometric coefficient of  $\text{CS}_2$ , and  $k = 3.0 \times 10^{-7} \text{ sec}^{-1}$ , so that

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{1 \times (3.0 \times 10^{-7})} = 2.31 \times 10^6 \text{ s} = \boxed{26.7 \text{ days}}$$

(F) The integrated first order rate equation is

$$\ln \left( \frac{[\text{CS}_2]_0}{[\text{CS}_2]} \right) = akt$$

so that, letting  $V$  denote the volume of the container,

$$t = \frac{1}{ak} \ln \left( \frac{[\text{CS}_2]_0}{[\text{CS}_2]} \right) = \frac{1}{1 \times (3.0 \times 10^{-7})} \ln \left( \frac{20/V}{7.5/V} \right) = 3.27 \times 10^6 \text{ s}$$

$$\therefore \boxed{t = 37.8 \text{ days}}$$

(G) We appeal to the same formula as in the previous part, letting  $m$  denote the remaining mass of  $\text{CS}_2$ ,

$$\ln \left( \frac{[\text{CS}_2]_0}{[\text{CS}_2]} \right) = akt \rightarrow \ln \left( \frac{20/V}{m/V} \right) = 1.0 \times (3.0 \times 10^{-7}) \times (60 \times 86,400)$$

$$\therefore \ln 20 - \ln m = 1.0 \times (3.0 \times 10^{-7}) \times (60 \times 86,400)$$

$$\therefore 3 - \ln m = 1.56$$

$$\therefore m = \exp(3 - 1.56) = \boxed{4.22 \text{ g}}$$



Was this material helpful to you? If so, please consider donating a small amount to our project at [www.montoguequiz.com/donate](http://www.montoguequiz.com/donate) so we can keep posting free, high-quality materials like this one on a regular basis.

Problems researched and solved by Lucas Monteiro Nogueira.  
Edited by Lucas Monteiro Nogueira.