Passage I (Answers 1-10)

1. C

Draw a skeleton structure that is as symmetric as possible.

Each nitrogen atom will contribute 5 valence electrons to the Lewis structure, while each hydrogen atom will contribute 1 electron.

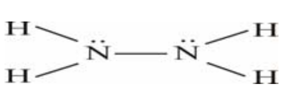
2N – 10 electrons
4H – 4 electrons

Total = 14 electrons

These 14 valence electrons must be distributed among the bonds and lone-pair electrons of the Lewis structure. When distributing the electrons, ensure that the octet rule is satisfied for each atom (There may be exceptions, where the octet is expanded. This normally occurs with elements in Period 3 and higher).

There may be several possible resonance structures, with multiple bonds (double or triple bonds). Choose the one that has the lowest *formal charge* (Note: formal charge = valence number - # non-bonding electrons – ½ # of bonding electrons).

The structure in **C** is the only on that satisfies all these rules.



2. D

Hydrazine is a neutral molecule, therefore it has an overall oxidation number of 0. The sum of the oxidation number of each atom in the molecule will give the molecule overall oxidation number.

The rules for assigning oxidation numbers states that H has an oxidation number of +1, except when bonded with metals to form metal hydrides. So,

$2 * N + 4 * H = 0$

$2 * N + 4 * (+1) = 0$

$\mathbf{N = -2}$

The answer is **D**.

3. D

$$1.0 \text{ mol } N_2H_4 \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2H_4} \times \frac{17 \text{ g } NH_3}{1 \text{ mol } NH_3}$$

= **34.0 g NH_3**.

The best answer is **D**.

4. D

The chemical formulae of the hydrazine hydrate is $N_2H_4 \cdot H_2O$. The molar mass of N_2H_4 is 32.0 g/mol; for H_2O, it is 18.0 g/mol. On a per mole basis, the mass of the hydrate is 50.0 g/mol. The percent by weight of hydrazine in this hydrate is

$$\frac{32.0 \text{ g/mol } N_2H_4}{50.0 \text{ g/mol } N_2H_4 \cdot H_2O} \times 100\%$$

= **32.0/50.0 x 100%**

The answer is **D**.

5. C

The reaction of Equation 2 is exothermic with a heterogeneous equilibria. So, only the gases will be included in the equilibrium constant: $K_{eq} = [N_2]^3[H_2O]^4$.

According to Le Châtelier's principle and the K_{eq} expression, only changes in the nitrogen and water concentrations will shift the equilibrium. An increase in pressure (using a smaller reaction vessel) will favor the reactants, since there are less gases on the reactant side. Catalysts are not included (typically) in the K_{eq} expression, so they will not influence the equilibrium.

Since this is an exothermic reaction, decreasing the temperature will favor the release of more heat. This will in turn promote the formation of more gaseous N_2 and H_2O. The best answer is **C**.

6. A

$$N_2(g) + 2H_2(g) \longrightarrow N_2H_4(l)$$

The reaction above shows the formation of 1 mole of N_2H_4. Therefore, the standard enthalpy change (ΔH^o) for this reaction is the same as the standard enthalpy of formation of N_2H_4 (enthalpy change accompanying the formation of 1 mole of substance in its standard state from the most stable forms of its elements in their standard states). From Table 1, the standard enthalpy of formation of N_2H_4 is 50.6 kJ mol^{-1}. The best answer is **A**.

7. B

Since ammonia reacts more vigorously with acids, hydrazine must be a weaker base (It is assumed that the reader knew previously that ammonia is a base). A weaker base will always have a smaller basicity constant (K_b). This means that the weaker base will not be easily ionized in solution, therefore it will react less vigorously with acids.
The best answer is **B**.

8. C

If the ΔG^o for the reaction is > 0, the reaction is not spontaneous, and it will not occur naturally under the given ambient conditions.

Since this is a formation reaction occuring at SATP, the $\Delta G^o{}_f$ value given in Table 1 for hydrazine may be used. In this case, $\Delta G^o{}_f$ = +149.2 kJ/mol > 0. Therefore, the reaction is indeed non-spontaneous and **C** is the best answer.

9. C

The entropy of gases are typically larger than liquids and aqueous solutions, and the entropy of liquids and aqueous solutions are typically larger than that of solids.

Since there are 7 moles of gases on the product side compared to 3 moles of liquid on the reactant side in Equation 2, the entropy should increase as the reaction proceeds forward, giving a positive entropy change.

Therefore **C** is the best answer.

10. A

Increasing the pressure of a gas, while maintaining the temperature constant will cause a proportional decrease in the volume (Boyle's Law).

So, 10 L x 1 atm/500 atm = **0.02 L**. The best answer is **A**.

Passage II (Answers 11-18)

11. B

The silica in Equation 1 is either reduced or oxidized (no combustion because no oxygen is being added and no carbonation because the final Si product does not have carbon).

The oxidation number of silicon in $SiO_2(s)$ is:

$$Si + 2(-2) = 0$$

$$Si = +4$$

The oxidation number of elemental Si(l) is 0.

To decrease the oxidation number (from +4 to 0), 4 electrons were gained by Si in $SiO_2(s)$. If electrons are gained, the atom is reduced. The best answer, then, is **B**.

12. C

Based on the passage, **C** is the best answer. The earth's crust is comprised of more than 25% silicon, therefore silicon is not a rare element. The last sentence in the passage states that silicon is non-reactive. The last sentence also states that silicon forms a diamond lattice, which implies that silicon crystallizes.

13. B

The size of the atoms in a covalent bond have a large influence on the strength of the bond. Larger atoms tend to make weaker compounds, with weaker bonds. Diamond is made up of carbon atoms. Since silicon is larger than carbon (Si is in Period 3, while carbon is in Period 2), the silicon lattice should be weaker than the carbon lattice of diamond. Therefore, **B** is the best answer.

14. B

All the responses show the abbreviated electronic configurations. Since Si is the second atom in Period 3 in the *p*-block of the periodic table, the 3*p* orbital should have only 2 electrons. Hund's rule states that the electrons should occupy the orbitals singly until each orbital has an electron. The configuration in **B** is the only one that satisfies these requirements.

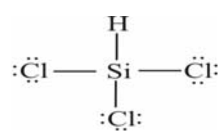
15. B

First, draw a Lewis structure to determine the number of VSEPR pairs (single, double, triple bonds, or lone pair electrons).

The total number of valence electrons in $SiCl_3H$ are:

Si = 4 electrons
3 * Cl = 3 * (7) electrons
H = 1 electron
Total = 26 electrons

Distribute the electrons in the skeleton of the structure, making sure that Si is the central atom. Make sure that the octet rule is satisfied for each atom in the structure and the formal charges are as close to zero as possible. The structure is:



In this structure, the octet rule is satisfied for each atom. Also, the formal charges is zero on each atom (Note: formal charge = valence number - # non-bonding electrons – ½ # of bonding electrons).

Since there are 4 VSEPR pairs on the Si atom, it's geometry is tetrahedral, making **B** is the best answer.

16. B

Another element in the same group as potassium (K) would exhibit some of the same properties, and be a good substitute. Of the choices, only Na is in Group 1A as K. Therefore, **B** is the best answer.

17. D

Boiling points are significantly affected by the intermolecular forces between the molecules. Since there are no ions in $SiCl_3H$, there are no ionic forces. The electronegativity difference between Si and H is not large enough to promote significant hydrogen bonding. Weak van der Waals forces is the predominant force that affects the boiling point of $SiCl_3H$. Therefore **D** is the best answer.

18. C

Fractional distillation is a process that is used to separate substances based on differences in their boiling points. With that in mind and the fact that $SiCl_3H$ has a lower boiling point than the solid impurities, **C** is the most appropriate response.

Passage III (Answers 19-28)

19. B

The additional electron in the OCl^- polyatomic ion will be localized across the O–Cl bond, but will spend more time around the oxygen (O is more electronegative than Cl). This will essentially make the O–Cl bond stronger and shorter. Addition of H to OCl^- will delocalize the extra electron across 2 bonds, H–O–Cl. This will make the O–Cl bond longer and easier to break. This will increase the rate of reaction. The best response is then **B**.

20. D

The rate law for Reaction 3 is rate = $k[ClO_3^-][Br^-][H^+]^2$. According to this rate law, the rate is directly proportional to the square of the $[H^+]$. So,

$$\text{rate} \ \alpha \ [H^+]^2$$

When rate = 1.0×10^{-2} *M*/sec, the pH = 1. The definition of pH can be used to find the hydrogen ion ion concentration.

$$pH = -\log[H^+]$$
$$1 = -\log[H^+]$$

$$[H^+] = 0.1\ M$$

Doubling the pH to 2 gives

$$2 = -\log[H^+]$$

$$[H^+] = 0.01\ M$$

Doubling the pH from 1 to 2, decreased the $[H^+]$ to 1/10th of the original concentration. Since the rate is proportional to the square of the $[H^+]$, this decrease will cause the new rate to be $(1/10)^2 = 1/100$th of the original rate. Therefore, the new rate is

$$(1.0 \times 10^{-2}\ M/\text{sec})/100 = \mathbf{1.0 \times 10^{-4}\ \mathit{M}/sec}$$

The best answer is **D**.

21. C

Reaction 3 is a redox reaction in which Br^- loses electrons (oxidized) to ClO_3^- (reduced). When Br^- changes to Br_2, each Br species loses an electron. Since there are 6 Br's in the balanced equation, 6 electrons are transferred, in total. The best answer is **C**.

22. D

More information is needed to compare the rates of the two reactions. One needs to know the order of the reaction rate of Reaction 1 with respect to the reactants (not given in the passage). If the rate law was known for both reactions, the equilibrium expressions could be written, the the ratio of the K_{eq}'s could be found. To do that the concentrations of HOCl and H^+ would be needed. **D** is the best answer.

23. D

Based on the explanation provided in question **19**, addition of the hydrogen to oxygen to form HOCl, reduces the electronic attraction forces between the chlorine atom and the oxygen atom that is being transferred. This explains why the bond becomes longer, and easier to break, after the addition of the hydrogen. The best answer is **D**.

24. B

The size of the reacting species plays a significant role in determining the rate of a reaction. The species must collide with each other in a specific orientation to promote reaction. Large bulky groups will react slower, while smaller species will react faster, since it is easier for smaller groups to have the correct orientation necessary for reaction. Choices I and III are therefore correct in this case. **B** is the correct response.

25. A

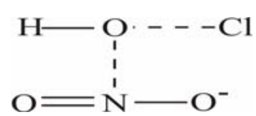
In this case (*Sequence III* of the last sequence of reactions), the equilibrium is heterogenous, so $H_2O(l)$ would not be included. Of all the choices, only **A** satifies Le Châtelier's principle: addition of more $SO_3(g)$ would shift the equilibrium to the right and increase the rate of $SO_3{}^{18}O^{2-}$ production.

26. D

The rate of a multi-stepped reaction is determined by the slow step, or the *bottle-neck* step. *Sequence II* is the slow step, so the rate law should be based on the reactant concentrations of this step. Note that if there are coefficients in the balanced reaction of the step, they must be included in the rate law as the exponents of the reactant concentrations (**this only applies to the rate law of each individual step in a reaction mechanism, not to the overall reaction**). Choice **B** satifies these requirements for *Sequence II*. (k_{II} is the rate constant for *Sequence II*).

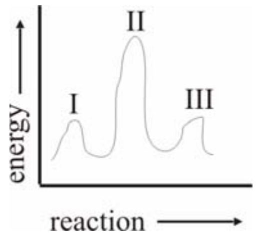
27. D

In NO_3^-, N is the central atom with all the O's bonded directly to it. Only choice **D** shows a transition that would make that structure possible.



28. B

Since *Sequence II* is the *rate-determining* step (slow step), it will have the highest energy requirement on the energy diagram. The two fast steps may or may not have the same energy requirement. More information is needed to determine that specifically. Only choice B shows *Sequence II* with the highest energy requirement and the other two sequences with lower energy requirements.



Passage IV (Answers 29-37)

29. A

When a solid dissolves in water, the process can be either endothermic or exothermic. The heat released is the enthalpy of solution. A change in the temperature will affect the equilibrium of the process through the enthalpy of solution. According to Le Châtelier's rules, an increase in temperature favors the formation of product, if the enthalpy change of the forward reaction is positive (> 0). In this case, the products are Pb^{2+} and NO_3^- ions. If an increase in temperature forms more of these products, it indicates that the enthalpy of solution is greater than zero. Choice **A** is the correct answer.

30. C

The molality is defined as

molality = number of moles of solute/number of kilograms of solvent

The molar mass of $Pb(NO_3)_2(aq)$ is 331 g/mol. The density of water is approximately 1 g/mL.

$$m = \frac{37.7\,g\,Pb(NO_3)_2}{100\,mL\,H_2O} \times \frac{1\,mol\,Pb(NO_3)_2}{331\,g\,Pb(NO_3)_2} \times \frac{1\,mL\,H_2O}{1\,g\,H_2O} \times \frac{1000\,g\,H_2O}{1\,kg\,H_2O}$$

= **1.14 *m***

Choice **C** is the best choice.

31. C

This question is asking for the freezing point depression induced by a 10.75 *m* solution of ethylene glycol. The freezing point depression is given as

FPD = $K_f m$, where m is the molality of the solution.

FPD = (-1.86°C-kg/mol) * (10.75 mol/kg) = **-20.0 °C**

The best answer is **C**.

32. A

There will only be one mole of ethylene glycol ($C_2H_6O_2$) in solution, but 3 moles of ions when lead nitrate ($Pb(NO_3)_2$) is dissolved in solution. Therefore, for two equal concentrations of the two solutions, the lead nitrate solution will lower the freezing point of water by a threefold extent compared to an ethylene glycol solution. Choice **A** is the best response.

33. C

Ethylene glycol is an alcohol with 2 hydroxyl groups (-OH). This compound will hydrogen bond with water, which will promote solubility of the ethylene glycol. So, like dissolves like. However, Table 1 shows that increasing the temperature has little effect on the solubility of the glycol. Therefore, the generalization that "the solubility of a solute doubles for every ten-degree rise in temperature" probably does not apply in this case. **C** is the best answer.

34. B

Ethylene glycol will hydrogen bond with water. Heating the resulting solution to reach boiling will require more energy to break these intermolecular force bonds, so that the vapor pressure is equal to the atmospheric pressure – a requirement for boiling. The hydrogen bonds reduce the vapor pressure above the solution, and increase the boiling point. **B** is the most appropriate response.

35. B

In a hypertonic, interstitial fluid, the fluid is more concentrated than the cellular fluid. Water will move, by osmosis, from the cellular fluid into the interstitial fluid, and the cellular fluid will become more concentrated. **B** is the best response.

36. D

According to Table 1, a saturated lead nitrate solution at 0^oC has a concentration of 37.7 g/100 mL. Equilibrating 39.0 g of lead nitrate in 100 mL of H_2O slowly over several days will produce an unstable, but saturated solution. In this case, the solution is supersaturated. Any sudden disturbances will initiate precipitation of the extra lead nitrate. **D** is the best answer in this case.

37. A

The mole fraction (*X*) is defined as

X = moles of solute/(moles of solute + moles of solvent)

Assume that there is 100 g of solution (solute + solvent). In this case, 10% will be lead nitrate (10 g) and 90% will be water (90 g). Convert all the gram masses to moles to determine the mole fraction.

$$X = \frac{10 \text{ g } Pb(NO_3)_2 \text{ x } 1 \text{ mol}/331 \text{ g}}{(10 \text{ g } Pb(NO_3)_2 \text{ x } 1 \text{ mol}/331 \text{ g}) + (90 \text{ g } H_2O \text{ x } 1 \text{ mol}/18 \text{ g})}$$

$= \mathbf{0.006}$

The best response is **A**.

Passage V (Answers 38-46)

38. B

If a reaction has an enthalpy change that is negative, it is exothermic. **B** is the best answer.

39. A

NH_3 is a base. It will react vigorously with a strong acid. All the acids presented as choices in this question are binary acids (hydrogen and another element only). Binary acid strength increases as size of the other element increases. In this case, HI is the strongest acid (I is very large), so ammonia should react most vigorously with it. Choice **A** is the appropriate choice.

40. C

The reaction of an acid with a base is a neutralization reaction. **C** is the correct response.

41. C

C is the only response that confirms the results shown in Table 1 and satisfies Le Châtelier’s principle.

42. A

The $FeO/Al_2K_2O_4$ mixture is a catalyst that is used to increase the rate of the reaction (Catalysts increase the rate of a reaction by facilitating the collision and reaction of the reacting species).

43. D

$NH_3(g)$, a base, will react with $H_2SO_4(aq)$, an acid, in a acid-base neutralization reaction. The balanced chemical reaction is

$$2NH_3(g) + H_2SO_4(aq) \longrightarrow (NH_4)_2SO_4(aq)$$

D is the best answer.

44. B

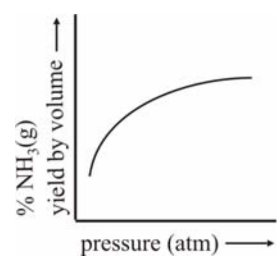
There is a large electronegativity difference between N and H in NH_3. This will create a large dipole moment in the molecule. The N will have a slight negative charge and the H, a slight positive charge. Oppositely charged atoms on neighboring atoms will be attracted to each other. The intermolecular attraction that results when a hydrogen atom (slightly positive) comes between two, small, highly electronegative atoms (N, in this case) is called a hydrogen bond. **B** is, therefore, the best answer. Note that hydrogen bonding is a specific type of dipole-dipole interaction. Typically, the term dipole-dipole interaction is used for atoms in a molecule that have an electronegativity difference, and none are hydrogen (eg. ICl).

45. B

The base should be able to accept protons (H^+ ions) or be nucleophiles (seeking positive species, or other species more positive than itself). This requirement eliminates immediately choices C and D. A stronger base will tend to consist of smaller atoms, that are very electronegative. In this case, the best choice will be $OH^-(aq)$. Choice **B** is the best response.

46. C

Table 1 shows that an increase in the pressure at 200°C increases the yield of $NH_3(g)$. However, the change (slope of a yield vs pressure curve) in the yield is not as large at higher pressures as it is at lower pressures. For example, changing the pressure from 1 atm to 100 atm engenders a change of 65.3% $NH_3(g)$. But, changing the pressure from 200 atm to 1000 atm delivers a change of only 12.5% $NH_3(g)$. The curve of choice **C** is the only one that illustrates the changes in the rate.



Passage VI (Answers 47-55)

47. A

According to Reactions 4 – 6, the CFC's must undergo photolysis to convert them to radical species before they can react with ozone. If the CFC's remain as gases, they cannot assist in ozone depletion. Therefore, **A** is the best answer. Note that the passage states that these compounds are inert, but they still undergo photolysis and deplete the ozone concentration.

48. A

Radicals are atoms that have unpaired electrons. As a result, they are extremely reactive. Cl· in Reaction 5 is very reactive because of the unpaired lone electron. **A** is the best answer.

49. C

In Reaction 3, M is formed in Step 1, but used immediately in Step 2. There is no net change in the amount of M in this reaction. Therefore, M is a reaction intermediate. Choice **C** is the most appropriate answer.

50. B

To determine the net reaction of Reactions 5 and 6, add the reactants and products of each reaction. Some cancellations will occur.

$$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$$

$$ClO\cdot + O \longrightarrow Cl\cdot + O_2$$

Sum:

$$Cl\cdot + O_3 + ClO\cdot + O \longrightarrow ClO\cdot + O_2 + Cl\cdot + O_2$$

$$\mathbf{O_3 + O \longrightarrow 2O_2}$$

Note that all the Cl· and ClO· were eliminated by cancellation. The best choice is **B**.

51. C

Steps 1 and 2 are reversible reactions (Note the rate constants k_1 and k_{-1} and the reactants and products involved in each). In most reaction mechanisms, reversible reactions are fast. The third step, Step 3, is most likely the slow step or the rate-determining step. Choice **C** is the best response.

52. D

The Δ*S* of the reaction can be found by taking the difference of the total entropy of the products from that of the reactants. Use the data provided in Table 1.

$$2O_3(g) \longrightarrow 3O_2(g)$$

ΔS = 3(205.0 J/mol·K) - 2(238.8 J/mol·K) = +137.4 J/mol·K

The best choice is **D**.

53. B

From Reactions 4 – 6, only choice **B** seems to be the most reasonable. For each mole of CFC consumed, 2 moles gaseous oxygen is produced.

54. C

Add the two reactions to find the net reaction:

$$O_2(g) \longrightarrow O(g) + O(g)$$

$$O_2(g) + O(g) \longrightarrow O_3(g)$$

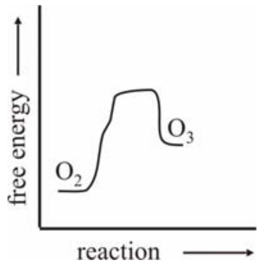
$$2O_2(g) \longrightarrow O_3(g) + O(g) \quad \textit{net reaction}$$

The free energy of the products are:

$$\Delta G_{f,products} = \Delta G_{f,O3} + \Delta G_{f,O} = (163.4\text{ kJ/mol}) + (230.1\text{ kJ/mol}) = 393.5\text{ kJ/mol}$$

The free energy of the reactants (oxygen) is 0 kJ/mol.

Therefore, the products should have a larger free energy value in the graph. In addition, the graph should show that the free energy is increasing as the reaction proceeds forward. Only choice **C** shows all these explicitly.



55. C

The sign of the reaction free energy change (ΔG) will indicate spontaneity of the reaction. A negative ΔG indicates reaction spontaneity; a positive value indicates that the reaction is non-spontaneous. Referring to question **54**, the reaction free energy change (ΔG = $\Delta G_{f,products}$ + $\Delta G_{f,reactants}$) is +393.5 kJ/mol. This reaction is not spontaneous because the free energy change is positive. Choice **C** is the best response.

Passage VII (Answers 56-

56. B

Since the $Zn(NO_3)_2(aq)$ is excess and $Na_2CO_3(aq)$ is limiting, the solution will be based on the amount of $Na_2CO_3(aq)$ to find the maximum amount of precipitate. The balanced chemical reaction is:

$$Zn(NO_3)_2(aq) + Na_2CO_3(aq) \longrightarrow ZnCO_3(s) + 2NaNO_3(aq)$$

Since all Na salts are soluble in water and most carbonates are sparingly soluble in water, the white precipitate is most likely $ZnCO_3(s)$.

From the passage, there is 2.0 mL of 0.1 *M* $Na_2CO_3(aq)$ solution.

$$2.0\ mL\ Na_2CO_3 \times \frac{1\ L\ Na_2CO_3}{1000\ mL\ Na_2CO_3} \times \frac{0.1\ mol\ Na_2CO_3}{1\ L\ Na_2CO_3} \times \frac{1\ mol\ ZnCO_3}{1\ mol\ Na_2CO_3} \times \frac{125.4\ g\ ZnCO_3}{1\ mol\ ZnCO_3}$$

$= \mathbf{0.03\ g}$

The best answer is **B**.

57. C

The oxidation number of an element in a compound will be influenced by the electronegativity of the atoms to which it is bonded. In this case, $Cl_2(g)$ is more electronegative than $I_2(s)$; $Cl_2(g)$ will attract electrons more strongly than $I_2(s)$ in a bond with Cu, changing the oxidation number of Cu. Therefore **C** is the best choice.

58. C

The reaction of $NaCl(aq)$ with $Cd(NO_3)_2(aq)$ is a metathesis reaction in which atoms or ions exchange partners. The balanced chemical reaction is:

$$2NaCl(aq) + Cd(NO_3)_2(aq) \longrightarrow CdCl_2(s) + 2NaNO_3(aq)$$

The chlorides of most transition metals are sparingly soluble. Note that the ion of Cd is Cd^{2+}, which means that the atom loses 2 electrons during ionic bonding. Therefore, 2 Cl atoms are needed to accept the electrons. The chloride of cadmium is $CdCl_2$ (see the balanced equation also). The best choice is **C**.

59. B

Mixing solutions of $AgNO_3(aq)$ and $NaCl(aq)$ would give the following reaction:

$$NaCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

The $AgCl(s)$ will dissociate slightly according to the following reaction:

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

$Cl^-(aq)$ is the conjugate base of a strong acid, $HCl(aq)$. This makes it a very weak base. Therefore, no reaction will occur between acidic $HNO_3(aq)$ and $Cl^-(aq)$. If $Cl^-(aq)$ is not consumed by the acid, then the amount of $AgCl(s)$ will remain unchanged. Choice **B** is the best response.

60. B

The most likely compound of Cd and S is CdS. The molecule will have an overall oxidation number of 0. The oxidation number of S is -2.

$$0 = Cd + (-2)$$

$$Cd = +2.$$

Choice **B** is the best response.

61. C

Zn will displace hydrogen gas from acids and steam. However, it will not displace hydrogen gas from cold water. **C** is the best response.

62. B

Addition of substances to an equilibrium system or changing the concentrations of substances already present will never change the actual value of the K_{sp}. Changing the concentrations or addition of substances that affect the existing reaction will give a Q_{sp} value, but the value of K_{sp} will remain the same. Only temperature changes will change the value of K_{sp}. The equilibrium will shift (concentrations will change), according to Le Châtelier's principle, to re-establish the equilibrium and the K_{sp} value.

Most hydroxides are slightly soluble in water. $Cu(OH)_2$ will dissociate by the following reaction:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

Addition of an acid (addition of H^+ ions) will consume OH^- ions. According to Le Châtelier's principle, more $Cu(OH)_2(s)$ will dissolve to re-establish the OH^- ion concentration and equilibrium. Response **B** is the best answer.

63. B

The presence of more ions in water will elevate its boiling point. $Zn(NO_3)_2(aq)$ will have 3 ions, which will elevate the boiling point of water more than $AgNO_3(aq)$, which will have only 2 ions upon dissociation. Choice **B** is the best choice.

64. D

From the activity series of metals, Cu will displace Ag from its compounds (Cu is more reactive than Ag). Ag will plate out as solid metal on the Cu strip. Cu will replace Ag in the nitrate. The balanced equation of this reaction is:

$$Cu(s) + 2AgNO_3(aq) \longrightarrow 2Ag(s) + Cu(NO_3)_2(aq)$$

oxidation #: 0 +1 0 +2

The oxidation numbers show that $Cu(s)$ lost 2 electrons (oxidized), while $Ag^+(aq)$ gained an electron (reduced). Note that in the nitrate, the metals are in ionic form. **D** is therefore the best response.

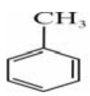
Passage VIII

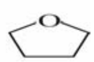
65. D

Table 1 shows that a larger percentage of the YT's dissolve in toulene compared to THF. Therefore, the YT's are more soluble in toulene than in THF, and **D** is the best choice.

66. A

The structures (based on information in the passage) of toulene and THF are given below.





Toulene

THF

Toulene has a larger ringed structure, with delocalized double bonds, which increases stability. THF is a 5-membered ring, which will experience larger ring strain. Based on the structures and this analysis, **A** is the best choice.

67. B

The abbreviated electronic configuration of Ti is [Ar]$4s^2 3d^2$. Typically, only electrons in the outer most shells and orbitals will participate in bonding. This holds true in this case, except that it is better to say that electrons in the most energetic orbital will form bonds. The most energetic orbital is the 3*d* orbital. **B** is the correct response.

68. D

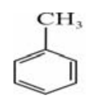
Simply heating a substance from 20°C to 700°C will not ionize it or promote a loss of protons. Heating certainly will not cause the formation of hydrogen bonds. The best conclusion is that volatile substances are vaporized due to the rise in temperature. **D** is, therefore, the best response.

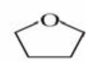
69. C

Elements in the same group typically exhibit similar properties. Ti is in group 4B. Of the choices given, only Zr is in group 4B. Choice **C** is the correct response.

70. A

The structures of toulene and THF are given below.





Toulene

THF

The oxygen in THF is bonded directly to carbon atoms. Since oxygen is more electronegative than carbon, there will be a dipole moment in this molecule, with oxygen being slightly negative. In water, hydrogen bonds will be formed with water molecules. Toulene does not have a dipole moment because the electronegativity difference between carbon and hydrogen is very small. So, hydrogen bonding will not occur between toulene and water. Hydrogen bonding increases the boiling point of a solution. Therefore, the THF solution should have the higher boiling point, making choice **A** the best answer.

71. B

The electronic configuration of the valence electrons in the unhybridized orbitals of oxygen are $2s^2 2p^4$. So,

↑↓ ↑↓ ↑_ ↑_
2*s* 2*p*

Hybridization mixes the unhybridized orbitals (imaginary) to form new hydridized orbitals. For oxygen, with 2 bonds, there will be 2 hybridized orbitals with one electron each for bonding and 2 hydridized oribitals with 2 electrons for the lone pairs. The carbons will provide the remaining electron needed to satisfy the octet rule in oxygen. So, 1 *s* orbital will mix with 3 *p* orbitals to give the sp^3 hybridization of oxygen.

↑↓ ↑↓ ↑_ ↑_
sp^3 hybrid orbitals

The two paired electrons will be lone pair electrons and the single electrons will form the bonds with carbon. The best response is **B**.

72. A

The principal quantum number of an element specifies the number of shells in the atom. The number of shells is then a qualitative measure of radius of the atom. **A** is the appropriate response.

73. B

The abbreviated electronic configuration of the Ti atom is $[Ar]4s^23d^2$. To make the titanium ion, Ti^{2+}, 2 electrons are lost from the Ti atom. Those two electrons will be lost from the most energetic orbital with valence electrons, 3*d*. Therefore, the abbreviated electronic configuration of the ion is $[Ar]4s^2$. Choice **B** is the best response.

Passage IX

74. B

Moving from left to right in a given group on the periodic table, the number of electrons in the outermost shell increases. These electrons are able to push the inner-most electrons closer to the positively charged nucleus, reducing the shielding effect of those inner electrons and the atomic radius (Shielding effect is a phenomenon in which the the inner electrons push the outer, valence electrons from the positive nucleus, reducing the tendency of the atom to accept electrons). That enables atoms on the right side of the periodic table to accept electrons easier than atoms on the left of the table. Electronegativity is defined as the ability of an atom to accept electrons. The electronegativity increases as the shielding effect decreases. Choice **B** is the best response.

75. A

Non-metallic atoms, like S and F, typically form covalent bonds. $SF_6(g)$ is a covalent compound. Covalent compounds do not normally conduct electricity and heat very well. Choice **A** is the best answer.

76. C

The period number of an element is a qualitative indicator of the size of the atom. Metal atomic size increases from top to bottom in the periodic table, as the valence electrons are pushed away from the nucleus by a larger number of inner electrons. Therefore, it will be very easy for those outer valence electrons to leave the atom and participate in ionic bonding. Of the choices provided, RbCl has the metal with the largest radius. So, Rb required the least amount of energy to lose electrons, making **C** the correst answer.

77. A

Nonmetals are on the far right side of the periodic table. Choice **A** is the correct answer.

78. A

When an electron is lost, the radius of the ion is typically smaller than the parent atom. Smaller covalent bonds are stronger and require more energy to break. Ionic bonds tend to be stronger than covalent bonds. Ionization energy is the energy required to liberate an electron from a gaseous ground-state atom. Electron affinity is the energy change when a gaseous ground-state atom gains an electron. For metals, it is easier to liberate electrons than from non-metals, therefore, the ionization energies of metals are typically low. The energy change is typically larger when electrons are gained by non-metals, so, the electron affinity is typically larger. Choice **A** is the most appropriate choice.

79. D

Ionic bonding typically occurs between metals and nonmetals; covalent bonding occurs between nonmetals. **D** is the best choice (It fits the question also: ionic compound, NaCl, then covalent compound, HBr).

80. B

The compounds with the most ionic character will be those that consist of elements that readily participate in ionic bonding, that is, they lose or gain electrons easily. Of the choices provided, Cs is the metal that loses electrons the easiest (due to the shielding effect of 54 inner electrons on 1 outer, valence electron) and Cl is the nonmetal halogen that gains electrons the easiest (due to its large electronegativity). Choice **B** is the most appropriate.

81. C

If HCl were an ionic compound then a 1 *M* solution would conduct electricity. Of the choices provided, only **C** is absolutely true of all ionic compounds, since they dissociate in solution to give charged species.

82. B

The compound with the greatest ionic character will have the largest forces of attraction between the constituent ions. Therefore, the melting temperature will be high. Similar to the explanation in question 80 on the ionic character of a compound, choice **B** is the best response.

Passage X

83. A

ppm by definition is 1000 g particle/1,000,000 L solution.

$$\text{ppm} = \frac{1.6 \times 10^{-7}\ \text{mol}\,Ca^{2+}}{1.0\,\text{L solution}} \times \frac{40.1\,\text{g}\,Ca^{2+}}{1\,\text{mol}\,Ca^{2+}} \times \frac{1{,}000{,}000\,\text{L solution}}{1000\,\text{g}\,Ca^{2+}}$$

= 0.006 ppm

The appropriate response is **A**.

84. A

The best choice is **A**. According to Reaction 1, boiling removes HCO_3^- from solution. HCO_3^- can dissociate to give a proton and a carbonate ion. The proton will make the water more acidic. Removal of HCO_3^- will make the water less acidic and increase the pH. Then, conversion of Ca^{2+} to $CaCO_3$ will decrease the solubility of $CaCO_3$.

85. A

CO_2 will react with water to give carbonic acid as shown below:

$$CO_2(g) + H_2O(l) \rightleftarrows H_2CO_3(aq) \rightleftarrows H^+(aq) + HCO_3^-(aq)$$

unstable

According to Le Châtelier's principle, a high level of atmospheric CO_2 will shift the equilibrium to the right, producing more $H^+(aq)$. This will make the water more acidic and lower the pH.

Then, the excess $H^+(aq)$ will react with $CaCO_3$ to give calcium ions, CO_2, and H_2O. This will increase the solubility of $CaCO_3$. The most appropriate response is **A**.

86. C

The molar volume of an ideal gas is 22.4 L/mol. Use the molar ratios from the balanced equation of Reaction 1.

$$11.2\ L\ CO_2 \times \frac{1\ mol\ CO_2}{22.4\ L\ CO_2} \times \frac{1\ mol\ CaCO_3}{1\ mol\ CO_2} \times \frac{100.1\ g\ CaCO_3}{1\ mol\ CaCO_3}$$

$= \mathbf{50.0\ g\ CaCO_3}$.

Choice **C** is the best response.

87. C

$HCO_3^-(aq)$ is an acidic solution and $Ca(OH)_2(aq)$ is a basic solution. Mixing basic and acidic solutions will give a neutralization reaction. **C** is the best answer.

88. B

Assume that the system is at equilibrium. $CaCO_3$ will dissociate into calcium and carbonate ions. Initially, there were no Ca^{2+} or CO_3^{2-} ions. Assume that the change in ion concentration, to reach an equilibrium state, is x. The concentration of Ca^{2+} can be determined by using an ICE chart and the K_{sp} of $CaCO_3$.

CONCENTRATION SUMMARY			
Equation: $\mathbf{CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq)}$			
Initial Concentrations (mol/L)		0	0
Concentration Changes (mol/L)		$+x$	$+x$
Equilibrium Concentrations (mol/L)		x	x

$K_{sp} = [Ca^{2+}][CO_3^{2-}] = (x)(x) = 4.8 \times 10^{-9}$.

$[Ca^{2+}] = x = \mathbf{(4.8 \times 10^{-9})^{1/2}\ M}$

The best answer is **B**.

89. D

The dissociation reaction of $CaCO_3(s)$ is:

$$CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Adding excess Ca^{2+} to the solution will cause the equilibrium to shift to the left to consume the excess Ca^{2+}. CO_3^{2-} will also be consumed. This will cause the $CaCO_3$ to precipitate. Note that the value of K_{sp} will not change. Instead, the concentrations of the reacting species will change to maintain the K_{sp} value. **D** is the best response.

90. B

The calcium ion is Ca^{2+}. It is not a monovalent ion (having only one plus charge). This ion has no electrons to offer oxygen. Therefore, the ion will not react with oxygen. Typically, hydrated bivalent cations (positively charged ions having 2 plus charges) of Group 2A metals do not make water acidic (except Be^{2+}). The only best choice is **B**: Ca^{2+} is neutral to water.

91. C

Two species are isoelectronic when they have the same electronic configuration. The abbreviated electronic configuration of Ca^{2+} is [Ar]. This is exactly the same electronic configuration as Ar. The calcium ion is isoelectronic with the argon atom. **C** is the best response.

Passage XI

92. D

Alkalinity suggests basicity. Only KOH is a base. Therefore, **D** is the best response.

93. B

The Lewis structures of CO_2 and CH_4 are shown below.

CO_2 **CH_4**

The double bonds of CO_2 are shorter and stronger than the C–H bonds of methane. There are two VSEPR pairs (all bonds) around the central carbon in CO_2. Therefore, the geometry is linear. Four VSEPR pairs (all bonds; no lone pairs) around the central carbon in methane means that the geometry is tetrahedral. The best choice is **B** (I and III).

94. C

Of the choices given, only glycine and methanol of choice **C** will be able to hydrogen bond with each other if they were both in the same solution. Both have a terminal
–OH group, with the oxygen being more electronegative than H to establish a dipole moment along that bond.

95. D

The most abundant isotope of carbon is carbon-12. Isotopes have the same number of protons and electrons, but different number of neutrons. The mass numbers are given in the name of the isotope. Based on that, carbon-14 has 2 more neutrons than carbon-12 (Note that the mass number indicates the total number of neutrons and protons in the nucleus of an atom or ion). Choice **D** is the best response.

96. A

Glycine is a carboxylic acid (-COOH functional group), methanol is an alcohol (-OH functional group attached to a methyl group), and potassium hydroxide is a base (-OH group bonded ionically to a metal cation). Methanol can either be an acid or a base, depending on what it reacts with. Methanol can even autoprotonate itself: one methanol molecule acts as the acid and donates a proton, while the other acts as a base and accepts the proton. The best response is **A**.

97. C

The molar ratio of HCl(*aq*) to H^+(*aq*) is 1:1. Therefore, $[H^+] = 0.01\ M$.

pH = -log[H^+] = -log(0.01) = **2**.

The best choice is **C**.

98. D

As mentioned in question **93**, the central carbon of methane has 4 bonds, no lone pairs, and so, 4 VSEPR pairs. To have the exact geometry, there must be four bonds and no lone pairs. That eliminates choices A and B. XeF_4 has a total of 36 valence electrons, and will have an expanded octet around Xe (it can accommodate extra electrons since it is in Period 5). There are 32 valence electrons in $SiCl_4$, and all were distributed in the Lewis structure. Si has four bonds (satisfies the octet rule), and no lone pair electrons around Si. The best response is **D**.

99. C

A very low pH membrane channel will be itself very acidic. Glycine would pass through this channel in the form of its conjugate base. Only the H bonded directly to the oxygen on the –COOH group is acidic. Loss of this H, gives the conjugate base, which has a negative charge. Choice **C** gives the conjugate base.

100. A

The oxygen acceptor will most likely be a nonmetal (eliminates Fe). Noble gases do not accept or lose electrons readily (eliminates He). H_2, as a stable molecule, will not readily accept electrons. Sulfur is the only element proposed that has a large enough electronegativity, and even has similar properties as oxygen, to act as an electron acceptor. **A** is the best choice.