

Annotated Solution

2000 USNCO National Exam Part I

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1 Solutions

1. Ions get their color from d orbital electron transitions. Therefore, only species with a partially filled d orbital will be expected to have color. Fe^{3+} has a d^5 configuration so it is expected to show color. Ni^{2+} has a d^8 configuration so it is expected to show color. Al^{3+} has no d electrons so it is not expected to show color. The answer is **C. I and II only**

2. It is known that **D. phosphorus** has to be stored in water since it spontaneously ignites with air at low temperatures. Lithium does not make sense since it reacts violently with water and bromine and mercury are both relatively stable liquids at room temperature.

3. First, we know that the initial solution is colored since Cu^{2+} has a partially filled d subshell. This reaction forms a famous complex, $\text{Cu}(\text{NH}_3)_4^{2+}$, which is soluble and has deep blue color. Therefore, we already know the answer is **C**. The precipitate formed at lower concentrations is $\text{Cu}(\text{OH})_2$ since the ammonia forms a basic solution.

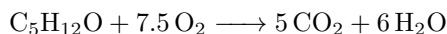
4. This is an oxidization reduction reaction where NO_3^- will be reduced to **NO**. H_2 cannot be formed since silver has a positive reduction potential. Therefore the answer is **A**.

5. The R_f value is the distance the substance travels divided by the distance the solvent travels. Using this formula gives $R_f = \frac{8.0-2.0}{10.0-2.0} = \mathbf{0.75}$ which is **B**

6. According to the graph, the absorbance at 0.050 M is 0.10 units. An uncertainty of .01 is $\frac{.01}{.10} = \mathbf{10\%}$ which is **B**.

7. A total of $\frac{0.124 \text{ g Ag}_2\text{S}}{247.8 \text{ g/mol}} \times \frac{215.7 \text{ g Ag}}{\text{mol Ag}_2\text{S}} = .108 \text{ g Ag}$ is in the ore, which corresponds to $\frac{.108}{1.50} = \mathbf{7.20\%}$ which is **B**.

8. The balanced reaction is



Therefore the answer is **C. 7.5 mol**.

9. Since there are two moles of hydroxide for each mole of $\text{Ba}(\text{OH})_2$, there must be twice the number of moles of benzoic acid than barium hydroxide. We have the equation

$$\frac{.200}{122.1} = 2 \times .120 \times x$$

which gives $x = \mathbf{6.82}$ mL which is **A**.

10. We want to produce $\frac{2.50}{70.9} = .0353$ mol of Cl_2 , which means $4 \times .0353 = .141$ mol of HCl

will be needed. This leads to $.141 \times 36.5 = 5.15$ g of HCl, and since the solution we are using is 36.0% HCl by mass, the total mass of the solution will be $5.15 \times \frac{100}{36.0} = \boxed{\text{B. 14.3}}$ g of solution.

11. We can compute the total concentration by computing the number of mols and the volume. The number of mols is $.020 \times .10 \times 2 + .050 \times .30 \times 3 = .049$ mol. The total volume is .070 L so the answer is $\frac{.049}{.070} = \boxed{\text{D. 0.70 M}}$

12. The formula for change in boiling point is

$$\Delta T = K_b \times m$$

However, we can replace m with $\frac{\text{g sample}}{\text{kg solvent} \times \text{molar mass}}$ to get a formula of

$$\Delta T = K_b \times \frac{\text{g sample}}{\text{kg solvent} \times \text{molar mass}}$$

and rearrangement gives

$$\text{molar mass} = K_b \times \frac{\text{g sample}}{\text{kg solvent} \times \Delta T}$$

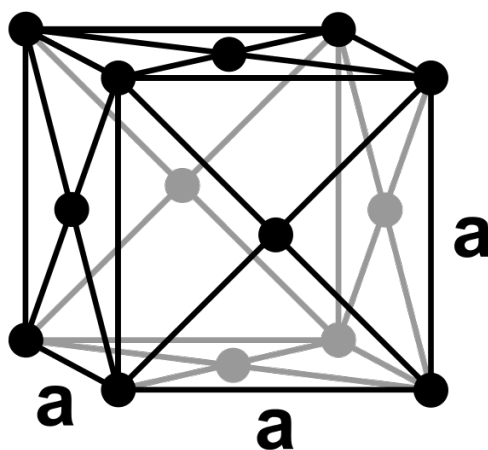
which matches with $\boxed{\text{C.}}$

13. This is an ideal gas law question. In order to apply it, we need to find the total mols of gas, which is $\frac{1.00}{4.00} + \frac{14.0}{28.0} + \frac{10.0}{30.0} = 1.08$ mol. Then, we can just apply the idea gas law with

$$P = \frac{nRT}{V} = \frac{(1.08)(.0821)(300)}{2.00} = \boxed{13.2 \text{ atm}}$$

14. Since metallic compounds have a sea of electrons, they are good conductors. Ionic compounds have high melting points since ionic bonds are very strong. Network covalent compounds have high melting points since breaking the lattice requires breaking the covalent bonds. $\boxed{\text{C. Molecular}}$ compounds satisfy both conditions since to boil them, we only need to overcome the intermolecular forces leading to a lower boiling point. They also have a low conductivity since they cannot form ions.

15.



If we look at a corner of a unit cell, we see that its nearest neighbors are the centers of adjacent faces. Since there are a total of 12 faces (4 per plane) the number of nearest neighbors is also $\boxed{\text{D. 12}}$. It is a good idea to remember the coordination numbers of common structures.

16. Based on partial pressures, we want to multiply the 300 by a factor that represents

$\frac{\text{H}_2 \text{ only}}{\text{H}_2 \text{ and H}_2\text{O}}$ which is equal to $\frac{740-20}{740}$ so the answer is **A.**

17. The normal melting point is located at the point where it transitions from solid to liquid at 1 atm. This is indicated by **B.**

18. Since the temperature goes up, we know that the reaction released heat. The amount of heat absorbed by the water is $254 \times 4.184 \times (26.01 - 23.73) = 2.42 \text{ kJ}$ and the heat absorbed by the calorimeter is $783 \times 2.28 = 1.79 \text{ kJ}$. Summing these up gives **D. 4.21 kJ evolved**

19. **C.** is incorrect since energy will be released when HCl gas is condensed.

20. The process is the sum of half of the first reaction reversed, half of the second reaction reversed, and the third reaction reversed. Therefore, $\Delta H = \frac{544.0}{2} + \frac{1648.4}{2} - 1118.4 = \text{B. } -22.2 \text{ kJ}$

21. From the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we want to choose the reaction whose ΔS° is the smallest in magnitude. This means minimizing the changes in phase, so the answer is **A.** since there are 3 mols of solid on both sides.

22. We want to compute the *BE* of the reactants minus the products. On the reactants side, we have one H-H and one O=O bond and for the products we have two O-H and one O-O bond. This gives $\Delta H = 436 + 499 - 460 \times 2 - 142 = \text{A. } -127 \text{ kJ}$

23. A reaction is spontaneous when ΔG° is negative. We know that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -38.3 + .113T$ so it is spontaneous when $T < 339 \text{ K}$, or 66°C so the answer is **C.**

24. Just apply

$$\Delta G^\circ = -RT \ln K = -(8.314)(298)(\ln(4.42 \times 10^4)) = \text{B. } -26.5 \text{ kJ/mol}$$

25. The instantaneous rate is the absolute value of the slope of the tangent line at the point. An estimation gives an answer of around **A. $4 \times 10^{-3} \text{ M} \cdot \text{sec}^{-1}$**

26. The half life is proportional with concentration for **A. Zero** order reactions. For example, it takes twice the amount of time to get from 4M to 2M as it does from 2M to 1M from the zero order half life equation, $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$.

27. Since 25 min is equal to 2.5 half lives, the ending concentration is just $40(0.5)^{2.5} = \text{C. } 7.1 \mu\text{Ci}$

28. From the first trial to the second, $[\text{CH}_3\text{C}(\text{O})\text{CH}_3]$ doubles and so does the rate, so its order is 1. From the second trial to the third, $[\text{I}_2]$ doubles but the rate does not change, so its order is 0. From the second trial to the fourth, $[\text{H}^+]$ doubles and so does the rate, so its order is 1. Combining this into a rate law equation gives **D. rate = $k[\text{CH}_3\text{C}(\text{O})\text{CH}_3][\text{H}^+]$**

29. From the Arrhenius equation

$$\ln(5) = \frac{E_a}{8.314} \left(\frac{1}{278} - \frac{1}{300} \right)$$

and solving gives **C. 50.7 kJ/mol**

30. If the second step were the rate determining step, then the first reaction would be at equilibrium, giving $[\text{N}_2\text{O}_2] = k[\text{NO}]^2$. Substituting gives

$$\text{rate} = k[\text{N}_2\text{O}_2][\text{H}_2] = k[\text{H}_2][\text{NO}]^2$$

so **C.** is the answer.

31. The equilibrium constant is the rate constant of the forward reaction divided by the reverse reaction (This can be derived by using the fact that the forward and reverse rates equal to each other at equilibrium). Therefore we have $\frac{2.3 \times 10^6}{k_{\text{reverse}}} = 4.0 \times 10^8$ which gives $k = \boxed{\text{B. } 5.8 \times 10^{-3} \text{ s}^{-1}}$

32. The reaction will only proceed right if

$$2.5 \times 10^{-2} = K > Q = \frac{[\text{C}]^3}{[\text{A}]^2[\text{B}]^2}$$

The only choice that satisfies this is $\boxed{\text{D.}}$

33. The amount of $[\text{OH}^-]$ that is ionized is $.050 \times 2.5\% = .00125 \text{ M}$ while the amount that is unionized is $.050 \times 97.5\% = .0488 \text{ M}$. The K_b value is equal to $\frac{[\text{ionized}]^2}{[\text{unionized}]} = \frac{.00125^2}{.0488} = \boxed{\text{C. } 3.2 \times 10^{-5}}$

34.

$$K_b = \frac{10^{-14}}{K_a} = 3.57 \times 10^{-7} = \frac{[\text{OH}^-][\text{HOCl}]}{[\text{OCl}^-]} = \frac{[\text{OH}^-]^2}{.65}$$

Solving this gives $[\text{OH}^-] = \boxed{\text{A. } 4.8 \times 10^{-4}}$

35. $\boxed{\text{D. HClO}_3}$ is one of the strong acids, while all of the others are weak.

36. The conjugate acid can be thought of as gaining hydrogen ion, so the answer is $\boxed{\text{B. H}_2\text{PO}_4^-}$

37. Since $\text{HCO}_3^- + \text{H}^+ \longrightarrow \text{H}_2\text{CO}_3$ is a titration between a weak base and a strong acid, an indicator in the acidic range will be most appropriate ($\text{p}K < 7$). Therefore we would want to use $\boxed{\text{A. methyl orange}}$

38.

$$K_a = 2.8 \times 10^{-8} = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{10^{-7.5}[\text{OCl}^-]}{.025} \implies [\text{OCl}^-] = .022 \text{ M}$$

$$.022 \times .150 = \boxed{\text{C. } 3.3 \times 10^{-3}}$$

39. This question is asking for the mixture such that $K_{\text{sp}} > Q = [\text{Ba}^{2+}][\text{F}^-]^2$. The only answer that satisfies this is $\boxed{\text{D.}}$ since $.020(.0020)^2 < 1.7 \times 10^{-7}$.

40. For this question, we need to remember the reduction potentials. Ag^+ has one of the highest reduction potentials while Zn^{2+} is much lower. Therefore, the oxidization-reduction reaction between Ag^+ and Zn will occur. Mg^{2+} will not be reduced since it has a very negative reduction potential (Mg is extremely reactive).

41.

$$\Delta G^\circ = -nE^\circ F = -2 \times (.80 - .34) \times 96500 = \boxed{\text{B. } -88.8 \text{ kJ/mol}}$$

42. We have the reaction $2 \text{Ag}^+ + \text{Cu} \longrightarrow 2 \text{Ag} + \text{Cu}^{2+}$ which has $Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$. Using the nernst equation, we have

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

Since $E_0 = .46$, we just need to compute

$$\frac{RT}{nF \log(e)} \log Q = \frac{8.314 \times 298}{2 \times 96500 \times 0.434} \log \left(\frac{1.00}{0.010^2} \right) = .0296 \times 4 = 2 \times .0591$$

so the answer is $\boxed{\text{D.}}$

43. Increasing the surface area of a solid only increases the rate since more of the electrode can be exposed to reaction. Therefore the answer is **B.**

44. Galvanizing is when one substance prevents another from reacting with its surroundings. In the given example, Iron is coated with Zinc to prevent the iron from rusting as Zinc is more reactive than Iron. Since Magnesium is extremely reactive, the iron pipe prevents reactions with water which is most similar to the process given so the answer is **A.**

45. Fe^{2+} will have a d^6 configuration. Using Hund's rule, each of the 5 orbitals will get one electron and one of those will have 2. Therefore, there are 4 orbitals with only one electron and **C. 4** unpaired electrons.

46. At first glance, the answer seems like Mg. However, Mg has a full s orbital while Al has an unpaired p electron, which is easier to remove. This is a similar effect to why elements with half filled p orbitals have an abnormally large ionization energy. Therefore, the answer is **B. Al**

47. **C. $3d, 4p, 5s$** is the correct order for filling electron orbitals. One can either use the diagonal rule to verify this or simply look at the periodic table.

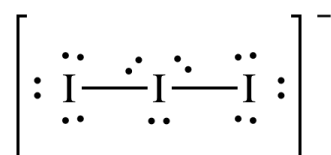
48. A cannot be correct since in going down a group, the ionization energy significantly decreases. B cannot be correct since in going across the periodic table with such small elements, the size change is very significant. C cannot be correct since successive ionization energies are significantly different. **D.** is correct since although the elements are moving across the periodic table, the change in size and effective nuclear charge is a lot less significant since d subshell electrons are poorly shielded.

49. Since radius decreases when moving right on the periodic table, we know that the elements must be in the order B, Be, Li, which only satisfies **A.** Na is larger than Li since it is lower in the periodic table.

50. Note that **A. SO_3** is isoelectronic to NO_3^- so they will have the same shape.

51. The formal charge is the number of valence electrons minus the number of electrons it currently has. N has 5 valence electrons and it currently has 4 electrons so the formal charge is **A. +1**

52.



Drawing the lewis diagram should give the figure above, which has 2 bonding pairs and 3 lone pairs, so the answer is **B.**

53. According to the VSEPR model, the lone pairs will repel each other, leading to smaller bond angles. Since NH_2^- , NH_3 , NH_4^+ have 2, 1, 0, lone pairs respectively, that is also the order of increasing bond angle, so the answer is **D.**

54. Carbon 1 has no pi bonds, so it is sp^3 . Carbon 2 has one pi bond, so it is sp^2 . Carbon 3 has two pi bonds, so it is sp . Therefore the answer is **C.**

55. This questions tests knowledge on molecular orbital theory. For 1, since the extra electron on O_2^- is antibonding, it will have weaker bonds than O_2 . For 2, since the removed electron on N_2^+ is bonding, it will have weaker bonds than N_2 . For 3, the first species is isoelectronic to N_2 which has a bond order of 3 and the second is isoelectronic to O_2 which has bond order of 2, so the first species will have stronger bonds. Therefore, the answer is **D. 2 and 3 only**

56. Since each corner of the structure represents a carbon, we know that there are 12 in total. We can find the degrees of unsaturation to be 7, which is 2 rings with 5 pi bonds in those rings. Therefore, the number of hydrogens is $12 \times 2 + 2 - 7 \times 2 = 12$ so the answer is **C. C₁₂H₁₂**
57. An alkyne has two degrees of unsaturation so it should follow the formula C_nH_{2n-2} which leads to the answer **D. C₄H₆**
58. There are two alcohols and one ether for a total of **B. 3** isomers.
59. **A. Acids** are resistant to oxidization since they are already at their highest oxidization state.
60. The answer is **D.** since acids and alcohols will undergo a condensation reaction to form esters.