## Annotated Solution 2020 USNCO Local Exam

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1. Start by writing the reaction. Because this is a combustion reaction, we know that the  $C_4H_{10}$  will react with  $O_2$  to produce  $CO_2$  and  $H_2O$  according to the following (unbalanced) equation:

$$C_4H_{10} + O_2 \longrightarrow CO_2 + H_2O$$

All the carbon and hydrogen on the products side comes from the  $C_4H_{10}$  on the reactants side. Therefore we can put a coefficient of 4 for  $CO_2$  and 5 for  $H_2O$ , as this allows 4 carbons and 10 hydrogens on both sides:

$$C_4H_{10} + O_2 \longrightarrow 4CO_2 + 5H_2O$$

Finally, we see that there are 13 oxygen atoms on the products side, so the reactants side must have 13 as well. This requires a coefficient of  $\frac{13}{2}$  for O<sub>2</sub> in the final balanced equation:

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$$

Now we analyze the equation PV = nRT for volume, as the question is asking us for a volume. We find that  $V = \frac{nRT}{P}$ . The question states that T and P are constant. Because R is the universal gas constant, it is constant as well. Therefore, volume is directly proportional to n, the number of moles of gas.

From the balanced equation, we see that the number of moles of  $CO_2$  will be four times that of  $C_4H_{10}$ ; therefore the volume will be four times greater as well. Therefore,

2.50 L C<sub>4</sub>H<sub>10</sub> 
$$\cdot \frac{4 \mod CO_2}{1 \mod C_4 H_{10}} = \boxed{10.0 \text{ L CO}_2}$$

Thus, the answer is C

**2**. This is just dimensional analysis using Avogadro's definition of a mole. For purposes of brevity, we will abbreviate pharmacolite as "P".

2.50 g P × 
$$\frac{1 \text{ mol P}}{216 \text{ g P}}$$
 ×  $\frac{6.02 \times 10^{23} \text{ molecules P}}{1 \text{ mol P}} = 6.97 \times 10^{21}$ 

However, this is the number of molecules of pharmacolite, and we need the number of hydrogen atoms in the pharmacolite. From the formula CaHAsO<sub>4</sub> · 2 H<sub>2</sub>O we see there are 5 atoms of hydrogen per pharmacolite molecule. Thus, the total number of hydrogen atoms is  $5 \times 6.97 \times 10^{21} = 3.48 \times 10^{22}$ , or D.

3. We can go backwards with dimensional analysis.

$$1.0 \times 10^6 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol}}{32 \text{ g}} = 3.1 \times 10^7 \text{ theoretical mol CH}_3 \text{OH}$$

At STP, we can use 22.4 L/mol. You can derive this using  $PV = nRT \implies \frac{V}{n} = \frac{RT}{P}$  at 273 K and 1 atm. Note that due to the low percent yield, the actual requirement of CO is greater than the theoretical requirement.

$$3.1 \times 10^{7} \text{ theoretical mol} \times \frac{100\% \text{ actual requirement}}{40\% \text{ theoretical requirement}} = 7.8 \times 10^{7} \text{ mol}$$

$$7.8 \times 10^{7} \text{ mol} \text{ CH}_{3}\text{OH} \times \frac{1 \text{ mol} \text{ CO}}{1 \text{ mol} \text{ CH}_{3}\text{OH}} \times \frac{22.4 \text{ L}}{\text{mol}} = \boxed{1.7 \times 10^{9} \text{ L}}$$

Thus, the answer is |C|.

4. We know that the moles before dilution must equal the moles after dilution. Thus, we can set up the equation with  $M_1 = 18.0$  M,  $M_2 = 0.55$  M, and  $V_2 = 250.0$  mL.

$$M_1 V_1 = M_2 V_2$$
  
(18.0 M) $(V_1) = (0.55 \text{ M})(250.0 \text{ mL})$   
 $V_1 = \boxed{7.6 \text{ mL}}$ 

Thus, the answer is C.

5. This question utilizes a lot of dimensional analysis. First, let's find the total mass per volume of the hydrogen peroxide in the solution by using the percentage by mass.

$$1.11 \ \frac{{\rm g\ solution}}{{\rm cm}^3} \times \frac{30.0\% \ {\rm H_2O_2}}{100\% \ {\rm solution}} = 0.333 \ \frac{{\rm g\ H_2O_2}}{{\rm mL}}$$

Now we can use this and the molar mass to find the concentration of  $H_2O_2$ .

$$0.333 \ \frac{\rm g}{\rm mL} \times \frac{1 \ \rm mol}{34.01 \ \rm g} \times \frac{1000 \ \rm mL}{\rm L} = \boxed{9.79 \ \rm M}$$

Thus, the answer is |A|.

**6**. We can set up multiple equations involving the mass. Let  $m_1$  represent the mass of K<sub>2</sub>S, and  $m_2$  represent the mass of KCl. The two equations we can set up are as follows.

$$m_1 + m_2 = 5.00 \text{ g}$$

$$\frac{39.10 \times 2}{39.10 \times 2 + 32.06} m_1 + \frac{39.10}{74.55} m_2 = 2.80 \text{ g}$$

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Solving these system of equations, we get  $m_1 = 0.99$  g and  $m_2 = 4.01$  g. Thus, the answer is

$$\frac{0.99 \text{ g}}{5.00 \text{ g}} \times 100 \% = \boxed{19.2\%}$$

Thus, the answer is B.

7. This is memorization of the colors of transition metals. Fe<sup>3+</sup>(aq) is yellow, Zn<sup>2+</sup>(aq) is colorless, Cu<sup>2+</sup>(aq) is blue, and  $\boxed{\text{Co}^{2+}(\text{aq})}$  is pink. Thus, the answer is  $\boxed{A}$ .

8. A buret is a precise volumetric piece of lab equipment, which allows for the estimation for one more digit. Thus, we can allow for one more digit beyond the marked 6.6. Thus,  $\boxed{6.63}$  is the correct answer, or  $\boxed{C}$ . When reporting numbers, the last digit is uncertain and can be estimated. Note that the buret reads top to bottom.

9. We can write the reaction, to start.

$$\operatorname{Zn}(s) + \operatorname{Cu}(\operatorname{NO}_3)_2(aq) \longrightarrow \operatorname{Zn}(\operatorname{NO}_3)_2(aq) + \operatorname{Cu}(s)$$

The reaction is a single displacement reaction, and we also know that Zn is more reactive than Cu. Thus, zinc reduces the copper sulfate, and the copper ion oxidizes the zinc, decreasing mass of the strip due to zinc's slightly higher molar mass. Thus, the answer is B.

10. Allotropes, by definition, are the various forms an element can take on. Carbon has graphite and diamond, oxygen has  $O_2$  and  $O_3$ , and phosphorous has multiple allotropes with different colors (i.e red, white, etc). Thus, the only element that does not have multiple allotropes is fluorine, or  $\overline{C}$ , which always takes the form  $F_2$ .

11. The key fact is that the dissolution and dilution of strong acids or bases tends to be exothermic. This eliminates A, B, and C. Thus, the answer is the sodium bicarbonate, or D.

12. We start with PV = nRT and solve for 1/n.

$$n = \frac{PV}{RT} \implies \frac{1}{n} = \frac{RT}{PV}$$

Now if we multiply by the mass m of the compound on both sides, we see that m/n is the molar mass M of the compound:

$$M = \frac{mRT}{PV}$$

If the flask is not sealed promptly, some of the compound will escape, so the measured m will decrease. This will decrease the calculated value of M, so the answer is A. If the compound dimerizes, the mass of the gases will increase. This is because the flask is connected to the atmosphere through the tiny hole on the aluminum foil. So the measured M will double. If the barometric pressure is assumed to be 1 atm when it is in fact greater, the P used in the equation will be smaller than it should be, so M will increase. If the V in the equation is smaller than the true volume, the calculated M will increase.

13. The rate of effusion can be determined by Graham's law, which states that

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

Letting compound A be oxygen, we know that  $M_A = 32$ , and  $r_B = \frac{r_A}{2}$ . Thus, we can simplify this to

$$2 = \sqrt{\frac{M_B}{32}}$$

Solving, we get  $M_B = 128$ . The only compound that has a molar mass relatively close to 128 is Xe, or D.

14. All of the answer choices are just isomers with four carbons, ten hydrogens, and one oxygen. Each has one hydroxyl group, allowing hydrogen bonding. We also know that boiling point is in associated with the strength of the intermolecular forces. We must then pick the molecule with the greatest intermolecular forces. Since 1-butanol is the least branched, molecules can come close together for maximum interaction. Thus, the answer is A.

15. Higher pressures tend to compress mass into a smaller volume. Lower temperatures also tend to reduce volume. From the phase diagram, we see that rhombic sulfur tends to be in the high pressure, low temperature region. Because density is inversely proportional to volume, rhombic sulfur is denser than monoclinic sulfur. This is C.

16. We can use the following relation to answer this question.

$$F \propto \frac{Q_+Q_-}{r^2}$$

where  $Q_+$  is the charge of the positive ion,  $Q_-$  is the charge of the negative ion, and r is the distance between the two ions. A larger Coulombic force between the ions will lead to a larger lattice energy. We know CaO will have the highest lattice energy because  $Q_+Q_- = 4$ . An increase by a factor of 4 is much more significant than any effects due to the distance r between the ions in most cases. Looking at the answer choices, we see the only answer that works is D.

17. The formula unit in each answer choice is NaX, where X is some halide. Thus each unit cell has 4 Na<sup>+</sup> and 4 X<sup>-</sup>. Its mass is [4(22.99) + 4(x)] amu. Since the unit cell is shaped like a cube, its volume is  $(462 \text{ pm})^3$ . Now we can use the density to find x, the mass of the halide.

$$\frac{[4(22.99) + 4(x)] \operatorname{amu} \times \frac{1}{6.022 \times 10^{23} \operatorname{amu}}}{(462 \operatorname{pm} \times \frac{1}{10^{10} \operatorname{pm}})^3} = 2.83 \operatorname{g cm}^{-3}$$
$$\frac{4(22.99) + 4x}{6.022 \times 10^{23}} = 2.83 \times (462 \times 10^{-10})^3$$
$$91.96 + 4x = 168$$
$$x = 19 \operatorname{amu}$$

The answer is |NaF| because a fluoride ion has the closest mass to 19 amu. This is |A|.

18. This is memorization of the unit cell rules. The sum of corner particles will contribute  $8 \times \frac{1}{8} = 1$ , the sum of face particles will contribute  $4 \times \frac{1}{2} = 2$ , and the center particle will contribute 1. Thus, the total sum is 1 + 2 + 1 = 4 or B.

19. The  $\Delta H_f$  represents forming one mole of a compound from elements in standard state. B and C can be eliminated because 8 moles of CaSO<sub>3</sub> are formed rather than one. D can be eliminated because it shows a reaction of CaO and SO<sub>2</sub>, which are compounds rather than elements in standard state.

For answer choice A, we see that Ca(s),  $S_8(s)$ , and  $O_2(g)$  are all in their natural states at 298 K and 1 atm (their standard states). The reaction forms one mole of  $CaSO_3(s)$ . Therefore, the answer is A.

**20**. We can set up equations in terms of T, then solve for it. For the ice cube, there are two energies involved. The energy used to melt the ice cube, and then heat up the resulting water. Thus, the total energy is

$$Q_{1} = Q_{\text{melt}} + Q_{\text{warm}}$$
$$Q_{\text{melt}} = 2.00 \text{ g H}_{2}\text{O} \times \frac{1 \text{ mol H}_{2}\text{O}}{18.01 \text{ g H}_{2}\text{O}} \times \frac{6010 \text{ J}}{1 \text{ mol H}_{2}\text{O}}$$
$$Q_{\text{melt}} = 2.00(4.184)(T - 0.0)$$

For the initial water, that will cool down because of the ice. Thus, the loss of energy will be as follows.

$$\begin{aligned} Q_2 &= 50.0(4.184)(T-25.0) \\ Q_1 + Q_2 &= 0 \text{ (conservation of energy)} \\ 2.00 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.01 \text{ g } \text{H}_2\text{O}} \times \frac{6010 \text{ J}}{1 \text{ mol } \text{H}_2\text{O}} + 2.00(4.184)(T-0.0) + 50.0(4.184)(T-25.0) = 0 \\ \text{Solving, we get } T &= \boxed{21.0^\circ} \text{ C, or } \boxed{A}. \end{aligned}$$

21. We can use the Clausius-Clapeyron equation to solve this problem. The equation is

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Let  $P_1$  and  $T_1$  refer to the point in time when the ethanol is at a temperature with a normal boiling point. Thus,  $P_1$  must be 1 atm. Thus, we need to solve for  $P_2$ . Because R is in joules, we must convert the  $H_{\text{vap}}$  into joules.

We now need to convert the temperatures into Kelvin.

$$T_1 = 78.3 + 273.1 = 351.4 \text{ K}$$
  
 $T_2 = 45.0 + 273.1 = 318.1 \text{ K}$ 

Thus, we can substitute to solve for  $P_2$ .

$$\ln\left(\frac{1 \text{ atm}}{P_2}\right) = \frac{-38600 \text{ J}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left[\frac{1}{351.4} - \frac{1}{318.1}\right]$$

Solving for  $P_2$ , we get

$$P_2 = \frac{1}{e^{1.38}}$$
$$P_2 = \boxed{0.25 \text{ atm}}$$

Thus, the answer is A

**22**. Writing the reaction, we get

$$\mathrm{C_2H_6} \longrightarrow 2\,\mathrm{C} + 6\,\mathrm{H}$$

With this, we can calculate  $\Delta H_{\rm rxn}$  by doing products – reactants.

$$\Delta H_{\rm rxn} = 718.4 \times 2 + 217.9 \times 6 - (-84.7)$$
  
 $\Delta H_{\rm rxn} = 2828.9 \frac{\rm kJ}{\rm mol}$ 

Now, we can write a second equation using our bond-dissociation enthalpies. Since breaking a bond is endothermic, we must do bonds broken minus bonds formed. In this case, no bonds are formed. One C-C bond and 6 C-H bonds are broken.

$$\sum BDE = \Delta H_{rxn}$$

$$6 \times 416 + BDE(C-C) = 2828.9$$

$$BDE(C-C) = \boxed{333 \frac{kJ}{mol}}$$

Thus, the answer is |B|

**23**. We can use the formula  $\Delta G = \Delta G^{\circ} + RT \ln Q$ . At equilibrium,  $\Delta G = 0$  and Q = K, so  $\Delta G^{\circ} = -RT \ln K_{eq}$ . From this we see that since  $\ln K_{eq}$  is positive and increasing at all temperatures 298 K to 350 K,  $\Delta G^{\circ} < 0$  and I is correct.

Next, we use the formula  $\Delta G = \Delta H - T\Delta S$ . From this we can derive  $\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T}$ . We have already shown that  $\Delta G^{\circ} < 0$ . Temperature *T* in Kelvin must be positive. Since  $K_{\text{eq}}$  increases with temperature, the reaction must be endothermic so that the forward reaction can reduce the increase in temperature by Le Chatelier's principle.  $\Delta H^{\circ}$  must then also be positive. Therefore, we see that  $\Delta S^{\circ} > 0$  and II is correct. Thus, the answer is I + II, which is C. **24.** At 1 atm and 100.0 °C, water reaches its boiling point. This means that it can turn into vapor if heat is added, or it can turn into liquid by releasing heat. Thus, the vaporization is reversible at 1 atm and 100.0 °C. Now let's think about the phase diagram of water. If we increase the pressure past 1 atm, water becomes a liquid, and the vaporization is no longer spontaneous. Thus, the answer is D.

**25**. From the reaction, we see that for each mole of  $O_2$  consumed, two moles of  $NO_2$  are produced. Thus we simply multiply by 2 to get  $0.084 \text{ M min}^{-1}$ , which is C.

**26**. From the rate law, the rate constant k is not dependent on either reactant OR product concentrations, although the rate itself is. Thus, the answer is D.

27. We can use the first order integrated rate law to solve this question, which is as follows.

$$[A] = [A]_0 e^{-kt}$$

When we want the half-life  $[A] = \frac{[A]_0}{2}$ . We also know that t = 4.1 min, so we can solve.

$$\frac{1}{2} = e^{-4.1k}$$
$$\ln\left(\frac{1}{2}\right) = -4.1k$$
$$\ln(2) = 4.1k$$

Solving for k, we get  $k = 0.17 \text{ min}^{-1}$ . We can substitute these values into the same rate law to solve again for t. However,  $[A] = 0.70[A]_0$  because after 30% composes we are left with only 70% of the compound.  $0.70 = e^{-0.17t}$ 

$$\ln(0.70) = -0.17t$$
 Solving for t, we get  $t = 2.1$  min. Thus, the answer is  $B$ .

**28**. We can use the equation below to solve for the activation energy  $E_a$ .

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

We need to convert the temperatures to Kelvin first. We also know that  $k_2 = 1.26k_1$ .

 $50+273.15=323.15~{\rm K}$ 

$$55 + 273.13 = 328.15$$
 K

Thus, we can substitute and determine our answer.

$$\ln\left(\frac{1.26k_1}{k_1}\right) = \frac{-E_a}{8.314 \text{ }\frac{\mathrm{J}}{\mathrm{mol} \times \mathrm{K}}} \left(\frac{1}{328.15 \text{ }\mathrm{K}} - \frac{1}{323.15 \text{ }\mathrm{K}}\right)$$

Solving for  $E_a$ , we get

$$E_a = \boxed{40.7 \ \frac{\text{kJ}}{\text{mol}}}$$

Thus, the answer is C.

**29**. The addition of the catalyst into the reaction will not shift the equilibrium, so the forward and backward reaction rates will increase at the same rate, and to the same degree. Thus, the answer is A.

**30**. We can start writing the rate laws for all of the reactions. The second step is ratedetermining and the first step can be approximated to be at equilibrium state. So the preequibrium approximation is used for the first step with an assumption of equal forward rate and backward rate.

$$k_1[\text{OCl}^-] = k_{-1}[\text{HOCl}][\text{OH}^-]$$
$$R = k_2[\text{HOCl}][\text{I}^-]$$

Because [HOCl] is present in both equations, but is not actually a reactant or a product (it is an intermediate), we can use it to substitute. Solving the first equation for [HOCl], we get

$$\frac{k_1[\text{OCl}^-]}{k_{-1}[\text{OH}^-]} = [\text{HOCl}]$$

Now substituting in the second equation, then we get

$$R = \frac{k_1 k_2}{k_{-1}} \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

Thus, the orders for  $[OCl^-], [I^-], [OH^-]$  are respectively  $\boxed{1, 1, -1}$ . This is answer choice  $\boxed{D}$ .

**31**. Adding more solid will not shift the equilibrium because solids are not part of equilibrium expressions. Neither will adding inert gas into a container with a constant volume because it is not part of the reaction. While A may look correct, it will only speed up the reaction, thus decreasing time to reach equilibrium. But this process does not change the equilibrium state itself. Thus, the answer is B. Since the reaction is endothermic, decreasing the temperature will favor the reverse exothermic reaction by Le Chatelier's principle.

**32**. First, let us write the reaction for  $NH_3$  and  $H_2O$ .

$$NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$$

From the given information, we know the following.

$$[OH^{-}] = 10^{pH-14} = 10^{-2.50}$$
  
 $pK_a + pK_b = 14$   
 $pK_b = 4.76 \rightarrow K_b = 10^{-4.76}$ 

We also know the following equation.

$$[OH^{-}] = \sqrt{C \times K_{b}}$$
  
$$10^{-2.50} = \sqrt{C \times 10^{-4.76}} \longrightarrow 10^{-5.0} = C \times 10^{-4.76}$$
  
$$10^{-0.24} = C$$

Therefore,  $C = \boxed{0.58 \text{ M}}$ . Thus, the answer is  $\boxed{D}$ .

**33**. We can set up the following equation, writing the concentrations as  $\frac{n}{V}$  where *n* is the number of moles.

$$K_{\rm f} = \frac{[{\rm Cd}(({\rm SCN})_4)^{2-}]}{[{\rm Cd}^{2+}][{\rm SCN}^-]^4} = \frac{\left(\frac{0.50}{V}\right)}{\left(\frac{0.50}{V}\right)^5}$$
  
1.0 × 10<sup>3</sup> = V<sup>4</sup> × (0.50)<sup>-4</sup>  $\longrightarrow$  1.0 × 10<sup>3</sup> × (0.50)<sup>4</sup> = V<sup>4</sup>  
Solving, we get  $V = \boxed{2.8 \text{ L}}$ , which is  $\boxed{C}$ .

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**34**. We can solve for  $[F^-]$  using the following equation.

$$K_{\rm sp} = [{\rm F}^{-}]^{2} [{\rm Ba}^{2+}]$$
$$[{\rm F}^{-}] = \sqrt{\frac{K_{\rm sp}}{[{\rm Ba}^{2+}]}}$$
$$[{\rm F}^{-}] = \sqrt{\frac{1.8 \times 10^{-7}}{5.0 \times 10^{-4}}}$$
$$[{\rm F}^{-}] = \boxed{1.9 \times 10^{-2} } {\rm M}$$

Thus, the answer is D.

35. We can write the reaction as follows.

$$H_3A \longrightarrow 3H^+ + A^{3-}$$

At the equivalence point, the number of moles of  $H^+$  equals the number of moles added of NaOH. Thus, by dimensional analysis

100.0 mL × 0.100 M trimesic acid × 
$$\frac{3 \text{ mol H}^+}{\text{mol trimesic acid}} = (0.500 \text{ M NaOH}) \times x$$

$$x = 60.0 \text{ mL}$$

However, remember that so far we have been talking about the equivalence point. From the graph, we see that the equivalence point occurs at 2V. Thus  $2V = 60.0 \text{ mL} \implies V = \boxed{30.0 \text{ mL}}$ . This is  $\boxed{D}$ .

**36**. We can write the reaction as follows.

$$\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6^{2+} + 4\operatorname{Cl}^- \Longrightarrow \operatorname{Co}\operatorname{Cl}_4^{2-} + 6\operatorname{H}_2\operatorname{O}$$

As we add  $Ag^+$ , the concentration of  $Cl^-$  will decrease due to precipitation of AgCl, and this will cause the equilibrium to shift to the left towards  $Co(H_2O)_6^{2+}$ . From this, we know  $Co(H_2O)^{6+}$  is pink, so I is correct. Also notice that when the solution is heated, the solution turns blue. Because we have found out that  $Co(H_2O)_6^{2+}$  is pink, this means that heating shifts the equilibrium to the right, away from  $Co(H_2O)_6^{2+}$ . By Le Chatelier's principle, if heating shifts the equilibrium right, the forward reaction must be endothermic. Thus, II is incorrect. The correct answer is I, which is A.

**37**. We can easily assign the oxidation states to everything but tungsten, and all oxidation states must sum to 0. The oxidation state for P is +5, +1 for each Na, -2 for each O, and x for each W.

$$0 = 3(1) + 1(5) + 12(x) + 40(-2)$$
$$0 = 8 - 80 + 12x$$
$$72 = 12x$$
$$x = 6$$

Thus, the answer is A

**38**. In order for charge to be consistent, we first need to balance  $H^+$  and  $H_2O$ . There are 3 oxygens on the reactants side, but 1 oxygen on the products side. Thus, the reaction becomes

$$\mathrm{H^{+}(aq)} + \mathrm{BrO_{3}^{-}(aq)} + \mathrm{Br^{-}(aq)} \longrightarrow \mathrm{Br}_{2}(aq) + 3 \mathrm{H}_{2}\mathrm{O}(l)$$

This now makes 1 H on the reactants side, and 6 H on the products side. We now add a 6 to the  $H^+$ . The reaction is now

$$6 \operatorname{H}^+(\operatorname{aq}) + \operatorname{BrO}_3^-(\operatorname{aq}) + \operatorname{Br}^-(\operatorname{aq}) \longrightarrow \operatorname{Br}_2(\operatorname{aq}) + 3 \operatorname{H}_2 O(l)$$

We see that on the products side there is no charge, but on the right hand side, there is a +4 charge. Because we already balanced the O, we have to add a coefficient of 5 to the Br<sup>-</sup>. When we do this, we now have 6 Br on the reactants side, and only 2 Br on the products side. Thus, we need to add a coefficient of 3 to balance the Br. The final reaction becomes

$$6 \operatorname{H}^{+}(\operatorname{aq}) + \operatorname{BrO}_{3}^{-}(\operatorname{aq}) + 5 \operatorname{Br}^{-}(\operatorname{aq}) \longrightarrow 3 \operatorname{Br}_{2}(\operatorname{aq}) + 3 \operatorname{H}_{2}O(1)$$

By looking at the answer choices, we see that |B| is the accurate statement, as  $6 = 3 \times 2$ .

You may also balance the equation by using the half-reaction method to get the correct answer.

**39**. We can determine the value of  $E_{\text{cell}}^{\circ}$  for each of the equations, and determine if it is positive or negative. If  $E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{ano}}^{\circ} > 0$ , then the process is spontaneous.

$$E_{\text{cell}}^{\circ}(I) = +0.52 \text{ V} - (-0.28 \text{ V}) = +0.80 \text{ V}$$
  
 $E_{\text{cell}}^{\circ}(II) = -0.28 \text{ V} - (-0.34 \text{ V}) = +0.06 \text{ V}$ 

Both Option I and II have a positive  $E_{cell}^{\circ}$ , so the correct answer is |I + II|, or |C|

40. We can set up the below equation to solve for the number of moles, and then convert via dimensional analysis.

$$Q = It = nF$$
  
(0.35 A)(1300 s) = n(96500 C/mol)

Solving for n, we get

$$n = 4.7 \times 10^{-3} \text{ mol } e^{-3}$$

In the anode, oxidation will occur and solid copper mass will be lost by the following reaction.

$$\operatorname{Cu}(s) \longrightarrow \operatorname{Cu}^{2+}(aq) + 2e^{-}$$

Then we can do dimensional analysis to get the grams.

$$4.7 \times 10^{-3} \text{ mol } e^- \times \frac{1 \text{ mol } \text{Cu}}{2 \text{ mol } e^-} \times \frac{64 \text{ g}}{1 \text{ mol}} = \boxed{0.15 \text{ g}}$$

Thus, the answer is C.

**41**. Looking at the equations  $\Delta G^{\circ} = RT \ln K$  and  $E^{\circ} = -\frac{RT}{nF} \ln K$ , we see  $\Delta G^{\circ} = -nFE^{\circ}$ . Also note that we must flip the second half reaction so that the two half reactions will sum to the desired reaction, which means the first half reaction is on the cathode (reduction), the second one is on the anode (oxidation). By the lowest common multiple method, we see  $n = \operatorname{lcm}(2, 4) = 4$ .

$$\Delta G^{\circ} = -(2.08 - 1.23)(4)(96500) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \boxed{-328 \frac{\text{kJ}}{\text{mol}}}$$

Thus, the answer is |B|.

**42**. From the line notation, we see zinc (anode) is oxidized and silver (cathode) is reduced. So the half-reactions we need to find the overall reaction are

$$\operatorname{Zn}(s) \longrightarrow \operatorname{Zn}^{2+}(aq) + 2 e^{-}$$
  
 $2 \operatorname{AgCl}(s) + 2 e^{-} \longrightarrow 2 \operatorname{Ag}(s) + 2 \operatorname{Cl}^{-}(aq)$ 

In order to obtain these reactions, we must multiply the top half-reaction by -1 and the bottom by 2. Then we can add the half-reactions together.

$$Zn(s) + 2 AgCl(s) \longrightarrow Zn^{2+}(aq) + 2 Ag(s) + 2 Cl^{-}(aq)$$
  
 $E^{\circ} = +0.222 V - (-0.762 V) = +0.984 V$ 

Now we use the equation  $E = E^{\circ} - \frac{RT}{nF} \ln Q$ . From the half reactions we see that n = 2.

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$
$$Q = [Cl^{-}]^{2} [Zn^{2+}] = (0.50)^{2} (1.0 \times 10^{-4}) = 2.5 \times 10^{-5}$$
$$E = 0.984 - \frac{(8.3145)(298)}{(2)(96500)} \cdot \ln(2.5 \times 10^{-5}) = \boxed{+1.120 \text{ V}}$$

Thus, the answer is D

**43**. All is well-known for taking the oxidation state  $Al^{3+}$  since Al is a main group element with 3 valence electrons. Thus, the answer is A.  $V^{2+}$  and  $Fe^{2+}$  are both common ions. Sm generally becomes  $Sm^{3+}$ , but  $Sm^{2+}$  is also possible.

44. We first need to write the electron configuration of Cl.

 $[Cl] : 1s^2 2s^2 2p^6 3s^2 3p^5$ 

We see that in the *p*-subshells (with 3 orbitals each) there is a  $2p^6$  (3 fully filled orbitals) and  $3p^5$  (2 fully filled orbitals and 1 lone electron). Thus, the answer is 3 + 2 = 5, or D.

45. As we go from left to right ionization energy increases, and as we go from top to bottom, it decreases. However, <u>nitrogen</u> actually has a higher ionization energy than oxygen. This is because the electron ionized from oxygen is in a paired 2p orbital, so it experiences electron-electron repulsion and is easier to remove. However, all 2p electrons in nitrogen are unpaired with less electron-electron repulsion so they are relatively more difficult to remove. Thus, the answer is A.

46. When going from aluminum to gallium, the added electrons will begin to fill the *d*-subshells. As these electrons are added, they provide a weaker shielding affect against nuclear charge, which results in a significant increase in effetive nuclear charge  $Z_{\text{eff}}$ . Therefore, There is an increase in electronegativity from Al to Ga. Thus, the answer is C.

**47.** l = 0, 1, 2, 3 refers to the s, p, d, f subshells. n = 3, l = 3 thus refers to a 3f subshell. Additionally noting that the value of l can only range from 0 to n - 1 inclusive, there is no such subshell. Thus, the answer is B.

48. Writing out the  $\beta$  decay and electron capture reaction will make this a lot easier.

Thus, the answer is A

**49**. This is just the application of the VSEPR model by drawing Lewis structures.  $CF_4$  will have a tetrahedral geometry,  $COF_2$  is trigonal planar,  $SF_4$  is see-saw with 5 electron domains including 1 lone pair, and  $SOF_2$  is trigonal pyramidal with 4 electron domains including 1 lone pair. Thus, the answer is B.

50. Let's draw the molecular orbital diagram for  $O_2$ , with 6 + 6 = 12 valence electrons for us to place in the bonding and antibonding orbitals. Make sure to follow Hund's rule.



We count two unpaired electrons.  $\text{ClO}_2$  and NO each have an odd number of valence electrons and therefore 1 unpaired electron. The only answer left is  $[\text{SO}_2]$ , or [C].

**51**. We know that  $H_3PO_3$  is diprotic, which means that one H is not connected to O. This eliminates D. Also, we want to avoid any O–O single bonds, as these bonds are weak and unstable. We can see this weak bond in  $H_2O_2$  and other peroxides. This eliminates A and B, and we see that  $\overline{C}$  is the best answer.

**52**. Because of the multiple resonance structures of  $C_4O_4^{2-}$ , all C–C bonds are the same with a bond order between 1 and 2, the same idea is applied for all C–O bonds. The negative charges are also evenly distributed on all four oxygens. Thus, it must have the same C–C and C–O bond distance, respectively. Thus, the answer is A.

53. The key fact in this question is that CO is isoelectronic to  $N_2$ , which has  $6e^-$  in the bonding molecular orbitals of the valence shell as shown in the molecular orbital diagram below.



The bond order in N<sub>2</sub> can be calculated to be 3 by using the molecular orbital diagram and the following equation. Remember that this diagram does not show  $\sigma_{1s}$  and  $\sigma_{1s}^*$  orbitals.

Bond order =  $\frac{1}{2}$ (number of bonding  $e^-$  – number of antibonding  $e^-$ )

Since CO is isoelectronic to  $N_2$ , the bond order should be the same.

However, NO has one more  $e^-$  than CO. From the molecular orbital diagram, we see there is no space for this electron other than in an antibonding orbital. This weakens and therefore lengthens the bond in NO (bond order = 2.5). Thus, we can explain the bond length because there is one fewer valence electron, or A.

54. We can think about how many choices we have and then multiply them because they are independent events. The ammonia could be either *cis* or *trans*, and the bromine and chlorine could swap places. However, due to the planarity of the molecule, only 2 of the molecules are actually unique, while the other two can be superimposed to form the other. Thus, the answer is B.

**55**. We can identify the compounds to eliminate our choices. B is an acid anhydride, C is a hemiacetal, and D is a ketone in addition to an ether. Only A is an ester, the dehydration product of an acid and alcohol. More specifically, A is a lactone, which is a cyclic ester. Thus, the answer is A.

56. Chiral molecules rotate the plane of plane-polarized light. In order for a molecule to be chiral, it cannot have a plane of symmetry and an inversion center. A is obviously symmetrical. B has a plane of symmetry from the O to the opposite vertex of the hexagon. C has a plane of symmetry from O to OH. We see that D does not have a plane of symmetry so it must be the answer. Furthermore, D is chiral because since the OH comes out of the page, the mirror image of D is not the same as D.

57.  $(CH_3)_2S$ , a typical nucleophile, reacts with the electrophile  $CH_3I$  to give the substituted products with  $I^-$  as the leaving group as follows.

$$(CH_3)_2S + CH_3I \longrightarrow (CH_3)_3S^+ + I^-$$

Thus, the answer is B.

More specifically, this is a bimolecular nucleophilic substitution reaction  $(S_N 2)$ .

**58**. Since we see that this is a hydrocarbon with 5 carbons, we need to start thinking about forms of pentane. First let's draw regular pentane.

This is a fairly large hydrocarbon, so we can try a cyclic form. Drawing cyclopentane, we see that each carbon can only have two hydrogens. Otherwise, it would break the octet rule. Thus, the formula of cyclopentane is  $C_5H_{10}$ , so this does not work.

Another isomer we can try is isopentane, a branched isomer of  $C_5H_{12}$ .

Notice that if we started the branch from the third carbon instead of the second one, it would still be the same molecule as we can see by turning the molecule around its vertical axis. The final isomer of  $C_5H_{12}$  is neopentane. This is a branched isomer where one carbon is in the center and the other four branch out of it.



These are the 3 isomers of C<sub>5</sub>H<sub>12</sub>, and the answer is C.

You may also use the general formula of  $C_nH_{2n+2}$  for alkanes to exclude any cyclic or multiplebonded structures. And all three isomers above are called skeletal isomers since they differ in the skeleton of the carbon chain.

**59**. In electrophilic aromatic substitution, the hydrogen(s) on the benzene ring will be replaced by an electrophile, which is an electron acceptor. Higher electron density on the benzene ring will lead to faster electrophilic aromatic substitution. To compare the answer choices, we can use the concept of activating groups: activating groups will increase the electron density, while deactivating groups will decrease the electron density.  $-\text{OCH}_3$  has a very strong electron-donating conjugation effect (+C) which increases the electron density, and a strong withdrawing inductive effect (-I) due to the high electronegativity of oxygen. On balance, the +C effect is stronger and it becomes a strong activating group.  $-\text{CH}_3$  has a weak electron-donating hyperconjugation (+C) effect, so it is a weak activating group. -Br has a strong -C effect and a medium -I effect, so it is a strong deactivating group. We see that the strongest activating group is  $-\text{OCH}_3$ . Thus, the answer is  $\overline{C}$ .

**60**. The key distinction between unsaturated fats and saturated fats is that the unsaturated fats have carbon-carbon double bonds that cause bends, thus A is incorrect. The bends prevent them from packing close together and interacting. This indicates lower IMF's, which would be indicative of lower boiling points. However, B contradicts this statement, and must be incorrect. Unsaturated fats converts to saturated fats through catalytic hydrogenation (adding H<sub>2</sub> to the C=C bonds in the unsaturated fats), as shown in C. All fats contain oxygen in the glycerol esters so D is incorrect.