

# Annotated Solution

## 2019 USNCO Local Exam

Authors: Ritvik Teegavarapu and Harys Dalvi  
Proofreader and Editor: Dr. Qiang 'Steven' Chen

Created on November 1<sup>st</sup>, 2020  
Revised on April 7<sup>th</sup>, 2021

### 1 Solutions

1. In order to determine the mass percentage, we need to find the mass of carbon and the mass of the compound. Afterwards, we need to divide the mass of carbon by the mass of the total compound. Doing this for all, we get the following.

$$A) \frac{12.01 \times 1}{12.01 + 1.008 \times 4} \approx 74.9\%$$

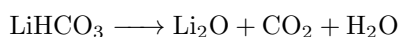
$$B) \frac{12.01 \times 2}{12.01 \times 2 + 1.008 \times 6} \approx 85.6\%$$

$$C) \frac{12.01 \times 4}{12.01 \times 4 + 1.008 \times 10} \approx 82.7\%$$

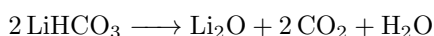
$$D) \frac{12.01 \times 8}{12.01 \times 8 + 1.008 \times 18} \approx \boxed{84.1\%}$$

Thus, the correct answer is  $\boxed{D}$ .

2. We must first write the reaction in order to understand what the question is asking.



Balancing the equation, we get



Now, all we have to do is some stoichiometry in order to find our answer.

$$0.50 \text{ mol LiHCO}_3 \times \frac{1 \text{ mol H}_2\text{O}}{2 \text{ mol LiHCO}_3} = \boxed{0.25} \text{ mol H}_2\text{O}$$

Thus, the correct answer is  $\boxed{A}$ .

3. We can use Dalton's Law of Partial Pressure to do this question. First, we need to determine the number of moles of each compound.

$$66 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44 \text{ g CO}_2} = 1.5 \text{ mol CO}_2$$

$$16 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32 \text{ g CO}_2} = 0.50 \text{ mol O}_2$$

Now, Dalton's Law of Partial Pressure states the following, where  $\chi_n$  is the mole fraction,  $P_t$  is the total pressure, and  $P_n$  is the individual pressures.

$$P_1 = \chi_1(P_t) \quad \text{and} \quad P_2 = \chi_2(P_t)$$

The mole fraction is the ratio of the moles of a certain element to the total number of moles to the compound. We can calculate that

$$\chi_1 = \frac{\frac{3}{2}}{2} = 0.75$$

$$\chi_2 = \frac{\frac{1}{2}}{2} = 0.25$$

We also know that  $P_t = 10$ . Thus, we can calculate  $P_1$  and  $P_2$ , and get our answer.

$$P_1 = 0.75 \times 10.0 = \boxed{7.5 \text{ atm}}$$

$$P_2 = 0.25 \times 10.0 = 2.5 \text{ atm}$$

Since  $\chi_1$  corresponds to  $\text{CO}_2$ , the answer is  $\boxed{C}$ .

4. The pressure and volume of the airbag comes from the  $\text{N}_2$ , as this is the only gas. First we must use  $PV = nRT$  to find the number of moles of  $\text{N}_2$ . Remember that the temperature  $T$  must be in Kelvin. Use  $R = 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$  so that the units given in the problem will cancel correctly.

$$T = 273.15 + 17 = 290. \text{ K}$$

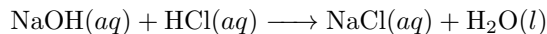
$$n = \frac{PV}{RT} = \frac{(1.20 \text{ atm})(16.0 \text{ L})}{(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) \cdot (290. \text{ K})} = 0.806 \text{ mol N}_2$$

Now we can use stoichiometry to find the mass of  $\text{NaN}_3$ .

$$0.806 \text{ mol N}_2 \times \frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \times \frac{65.02 \text{ g NaN}_3}{\text{mol NaN}_3} = \boxed{34.9 \text{ g NaN}_3}$$

The answer is  $\boxed{A}$ .

5.  $\text{NaOH}$  and  $\text{HCl}$  react completely in the reaction



In answer choice B, we must first determine the limiting reactant.

$$300 \text{ mL} \times 1.2 \text{ M NaOH} = 360 \text{ mmol NaOH}$$

$$600 \text{ mL} \times 0.6 \text{ M HCl} = 360 \text{ mmol HCl}$$

We see that there is no limiting reactant, so there will be 360 mmol  $\text{NaCl}$  in 900 mL water after the reaction proceeds to completion.  $\frac{360 \text{ mmol}}{900 \text{ mL}} = \boxed{0.4 \text{ M}}$ , so the answer is  $\boxed{B}$ . Checking A by the same method, we see that it yields only 0.2 M  $\text{NaCl}$ . Using  $C_1V_1 = C_2V_2$  we see that C yields 0.2 M  $\text{NaCl}$ , and D yields 0.24 M  $\text{NaCl}$ .

6. Adding a solute to the water will elevate the boiling point because the solute will lower the vapor pressure of the water, and so a higher temperature must be reached before the vapor pressure of the water matches the atmospheric pressure. The equation for calculating the temperature elevation of the boiling point is

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

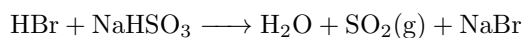
where  $m$  represents the molality. Molality can be defined as

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

The number of moles is defined as mass of the compound over molar mass. Because the mass of all the compounds remains constant throughout all the answer choices, decreasing the molar mass will increase the moles, thus increasing the molality, thus increasing the boiling point. Thus, the compound with the least molar mass will have the highest boiling point. By simple analysis of the choices, we can say that  $\boxed{\text{glyoxal}}$ , or  $\boxed{D}$  will have the lowest boiling point.

7. This is simply memorization of the flame tests. Because K is the only element that produces a pure violet flame test,  $\boxed{\text{KNO}_3}$  will be the only compound that produces a violet flame test, or  $\boxed{C}$ .

8. HBr reacts with  $\text{NaHSO}_3$  in the reaction

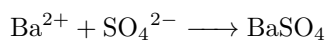


$\text{SO}_2$  is a colorless gas, so the answer is  $\boxed{A}$ .

9. Although  $\text{AgF}$  is a silver halide, it is soluble in water, which is the only exception to the silver halides group.  $\text{Ba}(\text{OH})_2$  is known as typical strong base with a medium solubility. Sulfates such as  $\text{CoSO}_4$  are generally soluble.  $\boxed{\text{CaF}_2}$  is highly insoluble. However, most fluorides are soluble except the compounds with some group IIA elements, so the answer is  $\boxed{A}$ .

10. Colorimetry is a technique which allows scientists to determine the concentration of a colored compound in solution. Since the solution has a visible purple color and absorbs light, colorimetry is viable. Additionally, since  $\text{KMnO}_4$  can act as an oxidizing agent (this is because Mn has a very high oxidation state (+7) in this compound; thus it must be reduced), it can be titrated with an reducing agent. Thus, the answer is  $\boxed{I + II}$ , or  $\boxed{C}$ .

11. The net ionic equation is



The calculated concentration of sulfate depends on the amount of  $\text{BaSO}_4$  that is measured. It is measured by comparing the mass of the crucible with the  $\text{BaSO}_4$  with the known mass of the empty crucible.

If the crucible contains a few drops of water when it is tared, the mass of the empty crucible will be taken as higher than it actually is. This means the calculated increase in mass due to the  $\text{BaSO}_4$  will be too low. The water drops are vaporized in the end, so the mass of  $\text{BaSO}_4(\text{s})$  measured will be lower than the actual value, then the sulfate concentration will be measured as too low. If some fine precipitate is not caught by the filter, there will be less  $\text{BaSO}_4$  measured than there should be. If some of the sulfate-containing solution spills, less  $\text{BaSO}_4$  will precipitate. Thus by elimination the answer is  $\boxed{B}$ . We know this is correct because the ashless filter paper will not increase the mass of the  $\text{BaSO}_4$  measured since it is completely changed into gases during the heating. The glass fiber filter will fail to do so, and so there will be a higher measured mass of  $\text{BaSO}_4$ .

12. In order to solve this problem, we will do a thorough analysis of the answer choices. Option D is obviously incorrect because you never touch lab equipment with your mouth. Option B is also quite incorrect, as you should never blow out anything with your mouth as particles could cross contaminate the residue. Option A is problematic because solution won't be sucked to the pipet if a pipet bulb or something equivalence is not used. Thus, only  $\boxed{C}$  is the correct answer, which is also the correct operation to dispense liquids using a volumetric pipet.

13. The two substances are situated at different temperatures, we have to use the extended version of Graham's Law of Diffusion. Let's derive this law according to kinetic molecular theory. According to kinetic molecular theory, the kinetic energy of a gas is directly proportional to the temperature in Kelvin.

$$E_K = \frac{3}{2}RT$$

From physics, we know that  $E_K = \frac{1}{2}mv^2$ . Solving for velocity, we get  $v = \sqrt{\frac{2E_K}{m}}$ . Now we can plug in kinetic energy to derive the equation for root mean square velocity:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

From this equation, we see that the rate of diffusion is directly proportional to the square root of temperature, and inversely proportional to the square root of molar mass. Thus, we can write an extended version Graham's law of Diffusion accounting for both factors:

$$\frac{r_1}{r_2} = \sqrt{\frac{T_1 M_2}{T_2 M_1}}$$

Since the effusion rates are the same,  $\frac{r_1}{r_2}$  is 1. We can now solve for  $M_2$ , assuming Compound 1 is methane.

$$1 = \sqrt{\frac{T_1 M_2}{T_2 M_1}}$$

$$T_2 M_1 = T_1 M_2$$

We say that  $T_1 = 150$  K,  $M_1 = 16$  g/mol, and  $T_2 = 600$  K. Substituting, we get

$$(600)(16) = (150)(M_2)$$

$$M_2 = 64 \text{ g/mol}$$

Thus, we need the compound that has a molar weight of 64 g/mol, which is  $\boxed{\text{SO}_2}$ , or  $\boxed{C}$ .

**14.** Nitrogen is far more electronegative than phosphorous and arsenic, according to our periodic trends. Thus, the resultant  $\boxed{\text{hydrogen bonding}}$  will be significantly stronger compared to the intermolecular forces with phosphorous and arsenic, which are unable to form hydrogen bonds. Thus, the answer is  $\boxed{D}$ .

**15.** The melting point of ionic solids is dependent on primarily two factors: the atomic radii of the ions, as well as the product of charges of the ions according to Coulomb's Law, which is expressed in the following equation.

$$F = k \frac{q_1 q_2}{r^2}$$

where  $q_1$  and  $q_2$  are the charges of the ions, and  $r$  is the distance between the ions. Because Mg has a charge of 2+, while Na and K have a charge of 1+, MgO must have the highest boiling point. The only answer choice that actually satisfies this is  $\boxed{\text{KBr} < \text{NaCl} < \text{NaF} < \text{MgO}}$ , or  $\boxed{A}$ . We can confirm this answer by looking at the ionic radius. From the periodic trends,  $\text{K}^+$  is larger than  $\text{Na}^+$ , and  $\text{Br}^-$  is larger than both  $\text{Cl}^-$  and  $\text{F}^-$ . Therefore, KBr will have the highest separation  $r$  (largest distance between the positive charged cation and negative charged anion) and the lowest lattice energy. Because Cl is larger than F, NaF will have a higher lattice energy than NaCl.

**16.** Metallic alloys can be substitutional, where some of X is replaced by Y or vice versa. This doesn't appear to be the case from the diagram. They can also be interstitial, where X occupies small holes between Y or vice versa. This also is not consistent with the diagram, so (A) can be eliminated.  $\boxed{\text{Molecular solids}}$  are discrete molecules in an ordered structure, which is consistent with the diagram so the answer is  $\boxed{B}$ . Ionic compounds are organized in lattice where ions are surrounded by opposite charge ions, which are not shown by the diagram. Network covalent solids are tight networks bonded together by covalent bonds, which is not shown in the diagram.

**17.** By analyzing the phase diagram, we can confirm that  $I$  is true because at 1 atm, the sublimation line from solid (s) to gas (g) is shown to go through below the triple point shown on the graph. We can also confirm that  $II$  is true because the point given is below the liquid-gas equilibrium line. Thus, both  $\boxed{I + II}$  are correct statements, which is answer choice  $\boxed{C}$ .

**18.** This unit cell has 8 corner cells, 6 face particles, and 1 center particle. By the unit cell rules, this means that X has a representative  $8 \times \frac{1}{8} = 1$  atom, Z has a representative  $6 \times \frac{1}{2} = 3$  atoms, and Y has  $1 \times 1 = 1$  atom. Thus the correct formula is  $\boxed{XYZ_3}$ , or  $\boxed{B}$ .

19. By conservation of energy, the sum of the lost energies must equal the total lost energy. We know that the total lost energy is 200. J. Thus, we can use the formula  $Q = mC\Delta T$  for both Fe and Ti.

$$Q_t = Q_1 + Q_2$$

For  $Q_1$  (Iron), the total energy lost is

$$Q_1 = 10.0(0.461)(T - 100.0)$$

For  $Q_2$  (Titanium), the total energy lost is

$$Q_2 = 10.0(0.544)(T - 100.0)$$

Now, we can sum all the energies to equal our total,  $-200.$  J.

$$-200. = (T - 100.0)(0.461 + 0.544)(10)$$

$$T = \boxed{80.1 \text{ }^\circ\text{C}}$$

Thus, the answer is  $\boxed{B}$ .

20. A, B, and C are comparing the same substance in different states of matter. We know that  $\boxed{\text{gaseous state}}$  has the most entropy, so  $\boxed{C}$  must be our answer. For answer choice D, there is only 1 mol of gas, while C has 2 mols.

21. Because the reaction is spontaneous at standard state, we know that  $\Delta G^\circ < 0$ . Thus, we can say

$$\Delta G = \Delta H^\circ - T\Delta S^\circ < 0$$

$$\Delta H^\circ < T\Delta S^\circ$$

$$\frac{\Delta H^\circ}{T} < \Delta S^\circ$$

Thus,  $\boxed{\Delta S^\circ > \frac{\Delta H^\circ}{T}}$ . Also, since the reaction is endothermic,  $\Delta H^\circ > 0$  so  $\boxed{\Delta S^\circ > 0}$ , thus the answer is  $\boxed{A}$ .

22. We can use the definition of internal energy change  $\Delta U$  in order to answer this question. We know that at constant pressure, the following equation holds true.

$$\Delta U = Q_P + W = \Delta H + W$$

Thus, solving for  $\Delta U - \Delta H$  leaves us with  $W$ , which denotes  $\boxed{\text{work}}$ . Thus, the answer is  $\boxed{B}$ .

23. Let  $x$  be the standard enthalpy of formation of  $\text{SiF}_4(\text{g})$ . Using products minus reactants from the reaction and the table, we have

$$(x - 2 \cdot 285.8) - (-910.9 - 4 \cdot 320.1) = 4.6$$

Solving for  $x$  we get  $\boxed{-1615.1 \text{ kJ mol}^{-1}}$ , which is  $\boxed{B}$ .

24. We can calculate  $\Delta G$  by saying

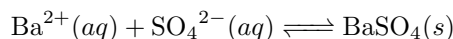
$$\Delta G = \Delta G^\circ + RT \ln Q$$

where  $R$  is the ideal gas constant,  $T$  is the temperature in Kelvin, and  $Q$  is the reaction quotient. At equilibrium,  $\Delta G = 0$  and  $Q = K$ .

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

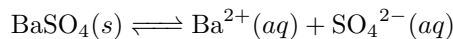
However, we have to pay attention to the reaction. The reaction given in the problem is



The value of  $K$  for this reaction is products over reactants (ignoring solids and liquids)

$$K = \frac{1}{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}$$

However, the value of  $K_{\text{sp}}$  refers to a different reaction (based on the definition of  $K_{\text{sp}}$ )



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

From this, we see that  $K$  for the given reaction is actually  $\frac{1}{K_{\text{sp}}}$ .

$$\Delta G^\circ = -RT \ln K = -RT \ln \left( \frac{1}{K_{\text{sp}}} \right) = RT \ln K_{\text{sp}}$$

$$\Delta G^\circ = \left( 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \times (298 \text{ K}) \times \left( \ln \left( 1.1 \times 10^{-10} \right) \right) = -56800 \frac{\text{J}}{\text{mol}} \cdot \frac{1 \text{ kJ}}{1000 \text{ J}} = \boxed{-57 \text{ kJ mol}^{-1}}$$

Thus, the answer becomes  $\boxed{A}$ .

**25.** From the first column to the second column, we see that  $[\text{A}]_0$  multiplies by 3 and  $[\text{B}]_0$  multiplies by 2. The overall reaction rate multiplies by 12.  $3^1 \cdot 2^2 = 12$  is the only combination that works. Thus the reaction is  $\boxed{1^{\text{st}} \text{ order in A and } 2^{\text{nd}} \text{ order in B}}$ , and the answer is  $\boxed{D}$ .

**26.** For this question we use the integrated rate law for first order reactions.

$$\ln([\text{N}_2\text{O}]) = -kt + \ln([\text{N}_2\text{O}]_0)$$

First, we solve for  $k$ .

$$\ln 0.640 = -42.0k + \ln 0.900$$

$$k = 8.12 \times 10^{-3} \text{ min}^{-1}$$

When the reaction is 90% complete, there will be  $0.900 \text{ mol} \times (1 - 0.900) = 9.00 \times 10^{-2} \text{ mol N}_2\text{O}$  remaining. We are trying to find  $t$  at this point.

$$\ln(9.00 \times 10^{-2}) = -kt + \ln(0.900)$$

$$t = \frac{\ln(0.900) - \ln(9.00 \times 10^{-2})}{k} = \boxed{284 \text{ min}}$$

The answer is  $\boxed{D}$ .

**27.** Using an equation from the reference sheet we know that

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

So the factor of rate increase is associated with  $\frac{1}{T_1} - \frac{1}{T_2}$ . Now we can compare the temperatures after converting to Kelvin.

$$\frac{1}{50 + 273} - \frac{1}{60 + 273} = 9.30 \times 10^{-5}$$

$$\frac{1}{60 + 273} - \frac{1}{70 + 273} = 8.76 \times 10^{-5}$$

From this we see that the increase from  $60^\circ$  to  $70^\circ$  is  $\boxed{\text{less than}}$  that from  $50^\circ$  to  $60^\circ$ , so the answer is  $\boxed{A}$ .

28. An inhibitor does not shift the equilibrium of the reaction toward the starting materials, it only increases the time to reach equilibrium. However, inhibitors may bind to the enzyme and block the active site. This is known as competitive inhibition. Thus the answer is I only, or A.

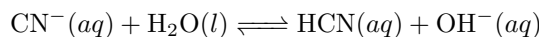
29. We have an irreversible reaction in the form  $A + B \longrightarrow$  products under conditions where  $[B] \gg [A]$ .  $1/[A]$  was linear in both plots, which is characteristic of a second-order reaction (see the integrated rate law for a second-order reaction) when  $[B]$  can be assumed not changing with time since it is in much excess. From the first plot to the second plot,  $[B]$  tripled, but the plot did not change. Therefore the reaction is zero order in B. Thus the rate law is  $\text{Rate} = k[A]^2[B]^0 = k[A]^2$ , or B.

30. Looking at the rate law, we see there is no  $[Cl^-]$ . From this we know there can be no  $Cl^-$  in the slow rate-determining step or in any previous step, eliminating (A) and (C). Also we see that the reaction is first order in  $H^+$ , so there must be exactly one  $H^+$  in the rate-determining step or a previous step. From this we can eliminate (D). This leaves only B, which we see is consistent with the rate law because there is one  $(CH_3)_3COH$  and one  $H^+$  but no  $Cl^-$  during and before the slow step.

Because the first step is a fast reversible reaction followed by a slow second step, we can confirm this with the pre-equilibrium approximation. If we assume the first step is in equilibrium, the second step will occur with  $\text{Rate} = k_2[(CH_3)_3C(OH_2)^+]$ . If we then use an equilibrium constant  $K = \frac{[(CH_3)_3C(OH_2)^+]}{[(CH_3)_3COH][H^+]}$  for the first step, note that  $K[(CH_3)_3COH][H^+] = [(CH_3)_3C(OH_2)^+]$ . Therefore, we can rewrite the rate of the rate-determining step as  $k_2K[(CH_3)_3COH][H^+]$ . Setting  $k_2K = k$ , we see this is equivalent to the given rate law.

31. Equilibrium means that the rates of the forward and backward reactions are the same. This means that concentrations are not changing, so the answer is A.

32. Ignoring the neutral sodium ion, the reaction is



Since  $CN^-$  is the conjugate base of  $HCN$ , it will have a  $K_b$  value of  $\frac{K_w}{K_a} = \frac{10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$ .

$$K_b = \frac{[OH^-][HCN]}{[CN^-]}$$

If we let  $x$  be the amount of  $OH^-$  produced by  $CN^-$  according to the above reaction, and we assume  $x$  is much less than 0.10 M, we get

$$K_b = \frac{x^2}{0.10}$$

Solving for  $x$  we find  $x = 1.4 \times 10^{-3} \text{ M} = [OH^-]$ . Now we must find the pH.

$$\text{pH} = 14 - \text{pOH} = 14 - (-\log [OH^-]) = 14 + \log(1.43 \times 10^{-3}) = \span style="border: 1px solid black; padding: 2px;">11.15$$

Thus, the answer is D.

33. By Le Chatelier's Principle, if pressure is increased, equilibrium will shift to reduce the pressure increase. From  $PV = nRT$  we see pressure is proportional to the number of moles of gases, so equilibrium will shift to fewer moles. Therefore, in order for the yield of products to not increase, products cannot have fewer moles than reactants. We see that the only choice where this is the case is A, as the products have fewer moles than the reactants in all the other choices. Thus, equilibrium will shift towards products (fewer moles) in the other reactions when pressure is increased.

34. From the definition of  $K_{sp}$ , we know that

$$K_{sp} = [\text{Cr}^{3+}][\text{OH}^-]^3 = 1.6 \times 10^{-30}$$

Now we must solve for the molar solubility using the given pH value. We know that

$$\text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$\text{pOH} = 14 - \text{pH} = 8.00$$

$$-\log([\text{OH}^-]) = 8.00$$

$$[\text{OH}^-] = 10^{-8.00}$$

Note that the molar solubility of  $\text{Cr}(\text{OH})_3$  is equal to the concentration of  $\text{Cr}^{3+}$ , because there is exactly one mole of dissolved  $\text{Cr}^{3+}$  for each mole of dissolved  $\text{Cr}(\text{OH})_3$ . Therefore, we must find  $[\text{Cr}^{3+}]$ :

$$K_{sp} = [\text{Cr}^{3+}][\text{OH}^-]^3$$

$$[\text{Cr}^{3+}] = \frac{K_{sp}}{[\text{OH}^-]^3} = \frac{1.6 \times 10^{-30}}{(10^{-8.00})^3} = \boxed{1.6 \times 10^{-6} \text{ mol L}^{-1}}$$

The answer is  $\boxed{D}$ .

35.  $K_p$  for the first reaction is

$$K_p = \frac{(P_{\text{SO}_2})(P_{\text{O}_2})^{\frac{1}{2}}}{(P_{\text{SO}_3})}$$

$K_p$  for the new reaction is

$$K_p = \frac{(P_{\text{SO}_2})^2(P_{\text{O}_2})}{(P_{\text{SO}_3})^2}$$

We see that since all coefficients were multiplied by 2, the new  $K_p$  is equal to the old one squared.  $(8.2 \times 10^{-4})^2 = \boxed{6.7 \times 10^{-7}}$ , or  $\boxed{A}$ .

36. Because  $\text{Na}^+$  is a spectator ion, we can write the net ionic equation for the dissociation of  $\text{RCOOH}$  without it:



This reaction has a  $K_a$  value where

$$\frac{[\text{H}^+][\text{RCOO}^-]}{[\text{RCOOH}]} = K_a$$

Before worrying about the titration, we know that  $[\text{RCOO}^-]$  and  $[\text{RCOOH}]$  are in a 1:1 mole ratio initially. Therefore

$$K_a = \text{H}^+ \implies \text{p}K_a = \text{pH}_{\text{initial}}$$

We see that the initial pH is 4.2, so the  $\text{p}K_a$  is also about 4.2 and  $II$  is correct.

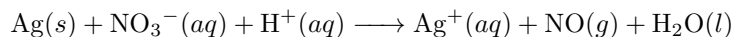
At the equivalence point, we know the number of moles of  $\text{NaOH}$  added equals the number of moles of initial  $\text{RCOOH}$ . We see from the graph that the equivalence point occurs when the number of moles is  $(0.5000 \text{ M})(7.50 \text{ mL}) = 3.75 \times 10^{-3} \text{ mol}$ . We also know that the mass of  $\text{RCOOH}$  is less than 0.500 g in the 1.000 g of mixture:  $\text{RCOOH}$  and  $\text{Na}(\text{RCOO})$  began in a 1:1 mole ratio, but  $\text{Na}(\text{RCOO})$  has a higher molar mass and so will take a larger proportion of the 1.000 g mass. Approximating the mass of  $\text{RCOOH}$  to be 0.500 g, we get

$$M_{\text{RCOOH}} = \frac{0.500 \text{ g}}{3.75 \times 10^{-3} \text{ mol}} = 133 \text{ g mol}^{-1}$$

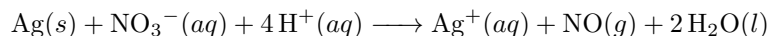
This is not within 5% of  $265 \text{ g mol}^{-1}$ , so  $I$  is false. Therefore the answer is  $\boxed{II \text{ only}}$ , or  $\boxed{B}$ .



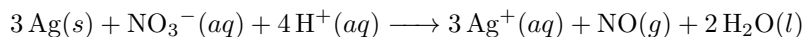
37. We are given



Balancing the nitrogen, hydrogen, and oxygen, we get

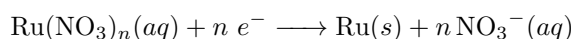


Finally, because the total charge must be the same (3+) on both sides, we have

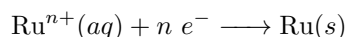


Thus, the ratio of  $\text{Ag}^+$  to  $\text{H}_2\text{O}$  is  $\boxed{3:2}$ , or  $\boxed{D}$ .

38. First, let's write the reaction, with the variable  $n$  being unknown.



The net ionic equation is



Note that a unit of one ampere (A) is equal to one coulomb per second (C/s). Also note that the magnitude of charge of one mole of electrons is referred to as one Faraday, where  $F = 96,500 \text{ C mol}^{-1}$ . This constant  $F$  can be found in the reference at the beginning of the olympiad exam. Now we can do dimensional analysis with an unknown variable  $n$ :

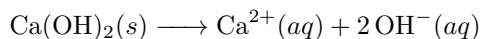
$$0.345 \text{ g Ru}(s) \cdot \frac{1 \text{ mol Ru}(s)}{101.1 \text{ g Ru}(s)} \cdot \frac{n \text{ mol } e^-}{\text{mol Ru}} \cdot \frac{96500 \text{ C}}{\text{mol } e^-} \cdot \frac{1 \text{ s}}{0.44 \text{ C}} \cdot \frac{1 \text{ min}}{60 \text{ s}} = 25.0 \text{ min}$$

$$12.5n = 25$$

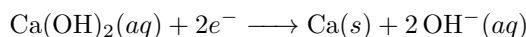
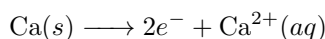
$$n = \boxed{+2}$$

Thus the answer is  $\boxed{A}$ .

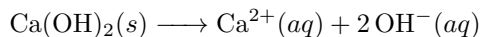
39. The dissolution reaction for  $\text{Ca}(\text{OH})_2$  is



In order to obtain this reaction, we see that we must flip the top reaction and keep the bottom reaction the same, which means the first one is on anode (oxidation) and the second one is on cathode (reduction).



Adding these together, we get



$$E^\circ = E_{\text{cat}}^\circ - E_{\text{ano}}^\circ = -3.02 \text{ V} - (-2.87 \text{ V}) = -0.15 \text{ V}$$

Now we use the equation

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

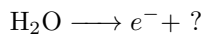
From the reaction we see that  $n = 2$ . When this reaction is at equilibrium,  $E = 0$  and  $Q = K_{\text{sp}}$ .

$$0 = E^\circ - \frac{RT}{2F} \ln K_{\text{sp}}$$

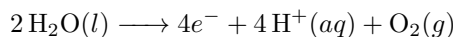
$$K_{\text{sp}} = \exp\left(\frac{2E^\circ F}{RT}\right) = e^{-11.7} = \boxed{8.4 \times 10^{-6}}$$

This is  $\boxed{C}$ .

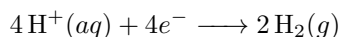
40. From the diagram, we see a positive end and a negative end on the external power source. Current flows from positive end to negative end, which means the negative charged electrons flow from the negative end to the positive end. The purpose of the sulfuric acid is to allow the electrons to flow through the solution, as pure water is a poor conductor. The electrons will enter the tube on the right from the negative end, and they will leave the tube on the right towards the positive end. Let's look at the tube on the right first, as electrons leave towards the positive end:



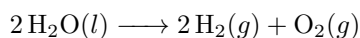
The negative charged oxygen in  $\text{H}_2\text{O}$  will lose electrons with  $\text{O}_2$  evolved as shown below.



Now there are spare  $\text{H}^+$  ions in the solution. In the left tube, this  $\text{H}^+$  can combine with electrons coming in from the negative end:



Adding these two equations together, we see that the net equation is



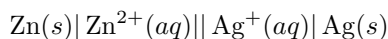
However, remember that the  $\text{O}_2$  is formed in the right tube as electrons leave water, and the  $\text{H}_2$  is formed in the left tube as electrons combine with water. The volume of gas in each tube is proportional to the moles of gases. The only answer with twice as much gas in the left tube is B.

41. From the overall reaction, we see that the first half reaction is on the anode (oxidation) and the second half one is on the cathode (reduction). Thus we have

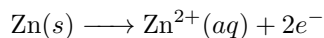
$$E^\circ = E_{\text{cat}}^\circ - E_{\text{ano}}^\circ = 0.337 - 0.222 = \boxed{0.115 \text{ V}}$$

The answer is D.

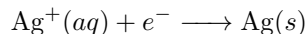
42. For this question, we must use the equation  $E = E^\circ - \frac{RT}{nF} \ln Q$ . This equation is available in the reference that comes with the exam.  $F = 96500 \text{ J V}^{-1} \text{ mol}^{-1} = 96500 \text{ C mol}^{-1}$  is the magnitude of charge of one mole of electrons.  $E^\circ$  is the standard cell potential. The question asks us to find  $E$ , the actual cell potential. We are given the cell



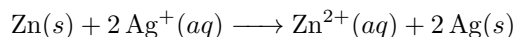
This is line notation. In line notation, the left side is the anode, which is oxidized. The right side is the cathode, which is reduced. The equation for the anode, where zinc is oxidized, is



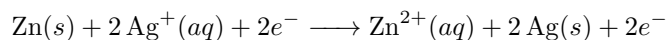
The equation for the cathode, where silver is reduced, is



The net equation is



In the equation  $E = E^\circ - \frac{RT}{nF} \ln Q$ ,  $n$  represents the number of moles of electrons that go from the anode to the cathode. From the reaction, we see  $n = 2$ .



The reaction quotient for this reaction is

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

In the problem, we are given  $T$ ,  $E^\circ$ ,  $[\text{Zn}^{2+}]$ , and  $[\text{Ag}^+]$ . Now we simply solve for  $E$  using  $R = 8.3145 \frac{\text{J}}{\text{mol K}}$ .

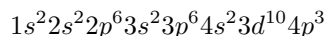
$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right)$$

$$1.562 - \frac{(8.3145)(298)}{(2)(96500)} \times \ln \left( \frac{(1.00 \times 10^{-3})}{(0.150)^2} \right) = \boxed{1.602 \text{ V}}$$

The answer is  $\boxed{A}$ .

**43.** The key fact to understand here is that the higher the frequency of a wave, the more energy it carries. Since wavelength is inversely proportional to frequency according to  $c = \lambda f$ , the wave with  $\lambda = 400 \text{ nm}$  will have  $\boxed{\text{more energy}}$  than the wave with  $\lambda = 800 \text{ nm}$ , which is only represented in answer choice  $\boxed{A}$ .

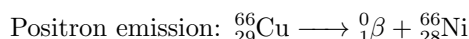
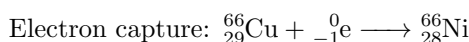
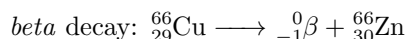
**44.**  $n = 3$  refers to the third shell and  $l = 1$  refers to a  $p$  subshell. Thus the question refers to the  $3p$  subshell. The electron configuration of arsenic is



We see that there are  $\boxed{6}$  electrons in the  $3p$  subshell, or  $\boxed{D}$ .

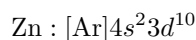
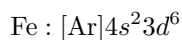
**45.** This is simply the application of the periodic trends. We know that ionization energy increases from left to right, and decreases from top to bottom. Because Ca is closest to the bottom left, it will have the least ionization energy. We also know, by the same logic, that N will have the most ionization energy because it is closest to the top left. Thus, the only option that satisfies this is  $\boxed{\text{Ca} < \text{Si} < \text{P} < \text{N}}$ , or  $\boxed{A}$ .

**46.** Let's write down the products of each decay to see which is most reasonable.



Now we can compare the atomic mass of the product for each form of decay with the atomic mass of corresponding element on the periodic table to confirm which decay yields a stable isotope. For *alpha* decay,  ${}_{27}^{62}\text{Co}$  has an atomic mass number of 62, about 3 higher than the periodic table value of 58.93. For *beta* decay,  ${}_{30}^{66}\text{Zn}$  has an atomic mass number about 0.6 higher than the periodic table value of 65.38. For electron capture and positron emission,  ${}_{28}^{66}\text{Ni}$  has an atomic mass number about 3 higher than the periodic table value of 58.693. We can predict that the most possible option with a stable isotope produced is through  $\boxed{\textit{beta} \text{ decay}}$ , or  $\boxed{B}$ .

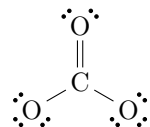
**47.** To determine if an element is paramagnetic or diamagnetic, we must see if it has any unpaired electron(s). A species is paramagnetic if there is at least one unpaired electron. A species is diamagnetic if all electrons are paired. In order to do this, we need to write the electron configurations.



Now we can make electron configuration diagrams for each element. The  $4s$  subshell is full for both elements. Since the  $3d$  subshell holds 10 electrons, it is full for Zn, but has four empty spaces for Fe. As stated by Hund's rule, there will be at least one electron in each orbital before the electrons start pairing in the orbitals. Therefore, there are four unpaired electrons in iron. Therefore Zn is diamagnetic and Fe is paramagnetic. So the answer is  $\boxed{B}$ .

48. Increasing atomic radii of metals with the same number of valence electrons leads to weaker metallic bonds because the atoms are farther apart. This makes liquids more volatile and decreases boiling point, fitting with A.

49. First, we need to draw the Lewis structure for  $\text{CO}_3^{2-}$ .



Notice that this is one of the three resonance structures: we could have picked any one of the oxygen atoms to have the double bond and the structure would be equally valid. Therefore all the bond lengths are equal, somewhere between a single and double bond. Additionally, the carbon has three bonding groups around it and no lone pairs, so the molecular geometry is trigonal planar. This means all three bond angles are  $120^\circ$ . The answer is C.

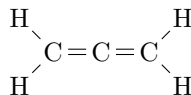
50. The trigonal pyramidal structure is formed when 1 lone pair is present, thus resulting with a total of four electron domains. Thus, this is just the application of the VSEPR model. By drawing out the Lewis-dot diagrams for all 4 choices, we can determine that there is only one answer with 3 bonding pairs and 1 lone pair, which is PCl<sub>3</sub>, or A.

51. Bond dissociation energy is dependent on the strength of the bond, as more energy is required to break the bond. Generally, as atomic size increases, the strength of the bonds will decrease since the atoms are further apart. However, for some molecules made by small atoms such as  $\text{F}_2$ , there is a more significant repulsion force caused by the closer lone pairs on both F atoms, which explains the exception of larger bond dissociation energy in  $\text{Cl}_2$ . Because  $\text{Cl}_2$  is larger in size compared to  $\text{F}_2$ , the repulsion forces are less significant in  $\text{Cl}_2$ , which is answer choice B.

Furthermore, the order of bond dissociation energy in halogens is  $\text{Cl}_2 > \text{F}_2 > \text{Br}_2 > \text{I}_2$ .

52. B does not satisfy the octet rule for the leftmost nitrogen with 6 electrons only, so it can be eliminated. C has two bonding groups and one lone pair for each nitrogen, indicating bent structure with a bond angle of around  $120^\circ$  or  $109.5^\circ$ , but the triangle geometry of the molecule limits the bond angle to be  $60^\circ$ , which causes a very large ring strain and makes the structure unstable. This leaves us with A and D. Both are reasonable structures and do contribute to the overall bonding (resonance structures), but A contributes more because oxygen is more electronegative, it makes more sense for oxygen to have a negative formal charge than nitrogen.

53. First, we need to draw the Lewis structure to determine the number of single, double, and triple bonds. This information will help us solve the problem because we know a single bond is one sigma bond, a double bond is one sigma bond and one pi bond, and a triple bond is one sigma bond and two pi bonds.



We know that, for  $s$  denoting the number of single bonds,  $d$  denoting the number of double bonds, and  $t$  denoting the number of triple bonds, the following is true.

$$\sigma = s + d + t = 4 + 2 = \boxed{6 \sigma} \text{ bonds}$$

$$\pi = d + 2t = \boxed{2 \pi} \text{ bonds}$$

By arithmetic, this is answer choice C.

54. Malleability allows the atoms in the metal to maintain their metallic bond, while still being able to move around. Thus, this means the electrons are free to move. This aptly fits the definition of delocalized electrons, or C.

55. Drawing the structure of 2-butene, we see that we can put the two methyl groups on the same side (*cis*) or on opposite sides (*trans*) of the C=C. This is geometric isomerism, so the answer is B. No other answers have different configurations that cannot be obtained by simply physically rotating the molecule.

56. Each carbon in cyclohexane has four single bonds around it. This means the molecular geometry around each carbon is tetrahedral, with bond angles close to  $109.5^\circ$ . This contributes to low strain energy because this is the ideal bond angle for a carbon with four single bonds, as opposed to a perfect hexagon with  $120^\circ$ . Additionally, the staggered C–H bonds will cause the hydrogens to be farther apart from each other. This will reduce strain because there is less repulsion between hydrogen atoms. Thus, the answer is C.

In organic chemistry, a staggered conformation is a chemical conformation of an ethane-like moiety abcX–Ydef in which the substituents a, b, and c are at the maximum distance from d, e, and f. This requires the torsion angles to be  $60^\circ$ .

57. Esters tend to be formed by an alcohol and an acid through dehydration, as esterification needs to be catalyzed by an acid or  $H^+$ . Methanol,  $CH_3OH$ , is an alcohol. Hydrochloric acid HCl is the acid that catalyzes the esterification of  $CH_3OH$ , so the answer is A.

58. There are four available spots on the benzene ring, as two are taken by  $CH_2CH_3$  and  $CH_3$ . Recall that these spots currently have hydrogen atoms. In a monosubstitution reaction, one hydrogen atom is replaced by bromine. Depending on which hydrogen atom is replaced by bromine, there are a total of 4 possible products, or D, since all four available spots are different.

59. Aromatic compounds follows the rule  $4n + 2$ , which describes the number of of electrons on the delocalized pi system ( $n$  is an integer here). (A) has 6 pi electrons, so it follows the rule for  $n = 1$ . (C) and (D) each has 10 pi electrons, so they follow the rule for  $n = 2$ . B has 8 pi electrons, so it does not follow the rule for any integer  $n$  and is not aromatic.

60. DNA is made of multiple nucleotides. Each nucleotide in DNA consists of a nitrogenous base, the sugar deoxyribose, and a phosphate group. The only part of this with phosphorus is the phosphate group. Phosphate has the formula  $PO_4^{3-}$  with a phosphorus atom surrounded by four oxygen atoms. Therefore, phosphorus is bonded only to oxygen, not to carbon or hydrogen. The answer is D.