

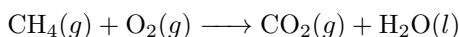
# Annotated Solution

## 2021 USNCO Local Exam

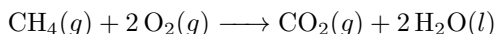
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1. First, let us write the reaction that is described in the reaction, with methane and excess oxygen forming carbon dioxide and water.



Balancing the equation, we get



Looking at the ideal gas law, we have the following.

$$PV = nRT$$

From this, we can state that the volume is directly proportional to the number of moles, or  $V \propto n$ . Thus, we can use the stoichiometric coefficients to determine the amount of moles of products.

$$1 \text{ mol CH}_4 \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} = 1 \text{ mol CO}_2$$

$$1 \text{ mol CH}_4 \times \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol CH}_4} = 2 \text{ mol H}_2\text{O}$$

Using the fact that volume is proportional to moles, that means there is  $\boxed{1.00 \text{ L CO}_2}$  and  $\boxed{2.00 \text{ L H}_2\text{O}}$ . Thus, the correct answer is  $\boxed{A}$ .

2. As the polymerization of propene is addition-based, which means there are no small molecules produced as byproducts. Thus, the mass of polypropylene must equal the mass of the propene. Now, the remaining steps are dimensional analysis given the initial mass.

$$3.50 \text{ g propene} \times \frac{1 \text{ mol propene}}{42 \text{ g propene}} \times \frac{6.02 \cdot 10^{23} \text{ molecules}}{1 \text{ mol propene}} = \boxed{5.01 \times 10^{22} \text{ molecules}}$$

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

3. Arbitrarily assume that there is 100.00 g of the compound. Thus, there is 61.71 g C, 4.03 g H, 16.00 g N, and  $100.00 - 61.71 - 4.03 - 16 = 18.26$  g O. Now, we can calculate the number of moles of each element.

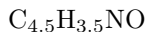
$$61.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.001 \text{ g C}} = 5.14 \text{ mol C}$$

$$4.03 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 3.998 \text{ mol H}$$

$$16.00 \text{ g N} \times \frac{1 \text{ mol N}}{14.007 \text{ g N}} = 1.14 \text{ mol N}$$

$$18.26 \text{ g O} \times \frac{1 \text{ mol O}}{15.999 \text{ g O}} = 1.14 \text{ mol O}$$

Dividing the least amount of moles, we have that the formula for the organic compound is of the following form.



Since we cannot have fractional subscripts, we multiply all of the subscripts by 2 to eliminate the 0.5 fractional part. Thus, the molecular formula for the compound is  $\boxed{\text{C}_9\text{H}_7\text{N}_2\text{O}_2}$ , or  $\boxed{B}$ .

4. First, let us calculate the number of moles of  $\text{CaBr}_2$  and  $\text{NaBr}$ . For  $\text{CaBr}_2$ , we have the following

$$0.1000 \text{ L} \times \frac{0.500 \text{ mol CaBr}_2}{1 \text{ L}} \times \frac{2 \text{ mol Br}}{1 \text{ mol CaBr}_2} = 0.100 \text{ mol Br}$$

For  $\text{NaBr}$ , we have the following.

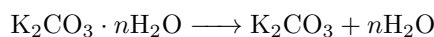
$$0.0500 \text{ L} \times \frac{1 \text{ mol NaBr}}{1 \text{ L}} \times \frac{1 \text{ mol Br}}{1 \text{ mol NaBr}} = 0.0500 \text{ mol Br}$$

Thus, we can calculate the molarity of the resulting solution by adding the moles of  $\text{Br}$  and divide by the total volume.

$$\text{molarity} = \frac{0.100 + 0.0500 \text{ mol Br}}{0.1000 \text{ L} + 0.0500 \text{ L}} = \frac{0.150 \text{ mol Br}}{0.1500 \text{ L}} = \boxed{1.00 \text{ M}}$$

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

5. First, let us write the dissociation reaction for  $\text{K}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ .



Using conservation of mass, we can determine there are  $1.000 - 0.836 = 0.164 \text{ g H}_2\text{O}$ . Using stoichiometry to relate the masses of  $\text{K}_2\text{CO}_3$  and  $\text{H}_2\text{O}$ , we have the following.

$$0.836 \text{ g K}_2\text{CO}_3 \times \frac{1 \text{ mol K}_2\text{CO}_3}{138.205 \text{ g K}_2\text{CO}_3} \times \frac{n \text{ mol H}_2\text{O}}{1 \text{ mol K}_2\text{CO}_3} \times \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 0.164 \text{ g H}_2\text{O}$$

Solving for  $n$ , we get

$$\frac{18 \times 0.836 \times n}{138.205} = 0.164$$
$$n \approx \boxed{1.5}$$

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

6. Theoretically, the molality measured by using boiling point elevation and freezing point depression should be similar. Here, the value got by boiling point elevation is smaller than that from freezing point depression for an aqueous solution of a nonvolatile, monoprotic acid. Ionization of the acid is  $\boxed{\text{markedly exothermic}}$  can explain the discrepancy the best as there is more dissociation of the weak acid at low temperature. As colligative properties is independent of the identity of the particles, but just the number of the particles. More dissociation at a lower temperature will give a higher molality of the acid. Thus, the correct answer is  $\boxed{A}$ .

7. When substances are separated by fractional distillation, substance that distills first has the lowest boiling point. The lower the boiling point, the smaller the IMFs, and the higher the vapor pressure.  $\boxed{\text{Higher molar mass}}$  causes a larger London dispersion force, which results in higher boiling point generally. Thus, the answer of  $\boxed{A}$ .

8.  $\boxed{\text{Oxygen}}$ , silicon, aluminum, iron, and calcium are the top 5 most abundant (by mass) elements in the Earth's crust. Thus, the answer is  $\boxed{B}$ .

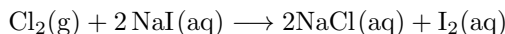
9. Note that since water is polar compound, polar compounds will be much more soluble in water than non-soluble compounds (hence the phrase "like dissolves like"). Looking at our answer choices, we see that  $\text{CO}_2$  and  $\text{O}_2$  are not polar, so A and C are eliminated. Comparing  $\text{H}_2\text{S}$  and  $\text{NH}_3$ , we see that  $\text{NH}_3$  will experience hydrogen bonding with water, as opposed to the  $\text{H}_2\text{S}$  that only experiences dipole-dipole interactions. Thus, the correct answer is  $\boxed{\text{NH}_3}$ , or  $\boxed{B}$ .

10. The key concept for this problem is that transition metals in compound will cause an overall coloration in

the compound in general, unless the transition metal ions have a fulfilled d subshell such as  $\text{Zn}^{2+}(\text{aq})$ . Thus, we must determine which of the following compounds does not contain transition metals. Doing a quick scan of the answer choices, we see that  $\text{RbIO}_4$  has no such transition metals, so the correct answer is  $\text{C}$ .

Moreover, the  $\text{MnO}_4^-$  in choice A  $\text{NaMnO}_4$  is dark purple, the  $\text{Cr}^{3+}$  in choice B  $\text{CrAsO}_4$  is green, the  $\text{CrO}_4^{2-}$  in choice D  $\text{BaCrO}_4$  is yellow.

11. When chlorine gas is bubbled into a colorless aqueous solution of sodium iodide, a reaction below occurs, which turns the solution yellow brown as  $\text{I}_2(\text{aq})$  is produced.



The reaction above is a reflection of the reactivity of halogens, down the group, the elemental form of the halogens ( $\text{X}_2$ ) is getting less reactive, harder to gain electrons to form the corresponding halides ( $\text{X}^-$ ). Thus, the correct answer is  $\text{D}$ .

12. The amount of water of hydration measured by this dehydration experiment is determined by the mass difference of the hydrated sample and the "dry" sample. So if some of the heated oxide (or a dry sample) is spilled from the crucible before it can be weighed, the mass lost is overestimated, thus resulting in a higher value of the amount of hydrated water. Thus, the correct answer is  $\text{D}$ .

For a further analysis, we will eliminate the other options. For choice A, it is very likely that not all of the hydrated water is removed, which results in a lower value. For choice B, this operation will not affect the result if the lid is also left off when weighing with the dehydrated oxide. For choice C, it will decrease the mass lost, resulting in a lower value.

13. Looking at the diagram, we see that there is movement in the particles, so it cannot be a solid. Additionally, the particles' movements are not so random that it can be represented by a gas or plasma. Thus, the correct answer is liquid or  $\text{B}$ .

14. First, let us write the ideal gas law equation.

$$PV = nRT$$

Re-expressing  $n$  as  $m/M$ , where  $m$  is the mass of the compound, and  $M$  is the molar mass of compound, we have the following.

$$PV = \frac{m}{M}RT$$

In the question, we are given the pressure (1.00 atm), the temperature  $23^\circ\text{C}$ , and the vapor density. Recognizing that the vapor density is simply  $\frac{m}{V}$ , we can rearrange the equation to solve for  $M$ , or the molar mass of the compound.

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

Substituting the given values, we have that

$$M = \frac{6.17 \frac{\text{g}}{\text{L}} \times (23 + 273 \text{ K}) \times 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}}{1.00 \text{ atm}}$$

Simplifying this, we get that

$$M = 152 \frac{\text{g}}{\text{mol}}$$

Thus, we need to calculate the molar masses of the compounds in our answer choices and determine which is closest to the value of  $M$  we got. We see that  $\text{C}_3\text{F}_6$  has the closest molar mass of  $150.03 \frac{\text{g}}{\text{mol}}$ , and thus, the answer is  $\text{A}$ .

15. When  $n$ -hexane ( $\text{C}_6\text{H}_{14}$ , bp =  $69^\circ\text{C}$ ) is vaporized, the main IMFs that must be overcome is London dispersion forces as  $n$ -hexane is nonpolar. Thus, the answer is  $\text{D}$ .

16. Recall the phase diagram of water, the solid-liquid equilibrium line has a negative slope, which indicates the thermal contraction of water. This, therefore, implies correctly that ice is less dense than liquid water. In another word, increasing the pressure will decrease the melting point. Thus, the correct answer is  $\text{A}$ .

17. Based on the information in the problem, we can list, At 366 K, we have the following.

$$P_{\text{CO}_2} + P_{\text{CO}} = 2.00$$

At 183 K, we have the following new relation for the partial pressure of CO.

$$P_{\text{CO}} = 0.90 - 0.25 = 0.65$$

According the ideal gas law, the partial pressure of CO at 366 K is two times of that at 183 K in the same container, we can get the following at 366 K.

$$P_{\text{CO}_2} = 2.00 - 0.65 \times 2 = 0.70$$

From this, we can calculate the mole fraction of CO<sub>2</sub> as follows.

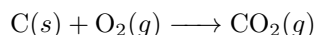
$$\text{mole fraction} = \frac{0.70}{2.00} = \boxed{0.35}$$

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

18. By the unit cell rules, we know that a corner cell only contributes  $\frac{1}{8}$  to the overall atom, and since there are 8 corners, we have a O atom from all the corners. We also know that the body atom will contribute 1 (since it is always present in any given constructed unit cell), so there are a total of 2 oxygen atoms.

In addition, the copper atom is shared between 2 atoms at any given point. Thus, there is a contribution of 4 from the copper atoms. Therefore, our chemical formula is Cu<sub>4</sub>O<sub>2</sub>, which simplifies to  $\boxed{\text{Cu}_2\text{O}}$ . Thus, the correct answer is  $\boxed{A}$ .

19. Since graphite is simply just carbon, we can write out the reaction described in the problem.



we can do dimensional analysis with the  $\Delta H_{\text{rxn}}$  and the initial mass of graphite. First, let us calculate the moles of graphite.

$$48.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} = 4.00 \text{ mol C}$$

Thus, we know for 4 mol C is equivalent to 1 mol rxn. Now, we can do the appropriate dimensional analysis.

$$\frac{-1574 \text{ kJ}}{\text{mol rxn}} \times \frac{1 \text{ mol rxn}}{4 \text{ mol C}} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = \boxed{-394 \frac{\text{kJ}}{\text{mol CO}_2}}$$

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

20. We can use the equation  $q = mc\Delta T$ , setting up two systems of equations, with  $q_1$  representing the heat absorbed by Sample A, and  $q_2$  representing the heat absorbed by Sample B. Since the same amount of heat is absorbed by both samples, we can set  $q_1 = q_2$ .

From the question, we know that  $m_a = 10.0 \text{ g}$  and  $\Delta T_a = 38 \text{ }^\circ\text{C}$ , and  $m_b = 20.0 \text{ g}$  and  $\Delta T_b = 23 \text{ }^\circ\text{C}$ . Thus, we can substitute this into our original equation and relate  $c_a$  and  $c_b$ .

$$q_1 = q_2$$

$$m_a c_a \Delta T_a = m_b c_b \Delta T_b$$

$$(10.0)(c_a)(38) = (20.0)(c_b)(23)$$

$$\frac{c_a}{c_b} = 1.2$$

$$c_a = 1.2c_b$$

Since  $c_a > c_b$ ,  $\boxed{\text{Sample A}}$  has the higher specific heat capacity. Thus, the correct answer is  $\boxed{A}$ .

21. We can first use process of elimination before determining the correct answer. Choice *D* is incorrect since we are unsure if the reactants or products have more gaseous moles. Since gases have the highest level of entropy, the side with the more gaseous moles will be more entropic. Since we do not have a clarification what the phase of the moles are, this does not necessarily have to be correct.

Choice *C* is incorrect because an endothermic reaction in which the temperature is increased will have stress placed on the reactant's side. By Le Chatelier's principle, the equilibrium will shift to the right towards the products, and thus, increasing the  $K_{\text{eq}}$ .

Choice *B* is also incorrect because since  $\Delta H > 0$  and  $\Delta S > 0$ , there is a transition temperature at which spontaneity of the reaction will transition from positive to negative. Since we do not know the transition temperature of the reaction, we cannot determine the spontaneity of the reaction.

Thus, choice **A** is the correct answer. This option is correct because a **well-insulated flask** indicates there is no loss of heat. Since  $\Delta H > 0$ , the reaction is endothermic, and heat will flow from the surroundings to the system, absorbed by the reaction and stored in the products. Thus, inserting a thermometer into the surroundings (i.e reaction mixture) will indicate a decrease in temperature.

22. We can use the Clausius-Clapeyron equation to solve this question, which is shown below.

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

The normal boiling point  $T_1 = 100 + 273 = 373\text{K}$  at normal atmospheric pressure  $P_1 = 1 \text{ atm}$ . At a different pressure ( $P_2 = 2 \text{ atm}$ ), there will be a different boiling point associated at the pressure.

We are also given that  $\Delta H_{\text{vap}} = 40.7 \frac{\text{kJ}}{\text{mol}}$ , and  $R$  as the ideal gas constant of  $8.314 \times 10^{-3} \frac{\text{kJ}}{\text{K} \times \text{mol}}$ . Substituting this into the aforementioned equation, we get

$$\ln\left(\frac{2.00 \text{ atm}}{1.00 \text{ atm}}\right) = \frac{40.7 \frac{\text{kJ}}{\text{mol}}}{8.314 \cdot 10^{-3} \frac{\text{kJ}}{\text{K} \times \text{mol}}} \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)$$

Solving for  $T_2$ , we get that  $T_2 = 394 \text{ K}$ , and converting this to Celsius, we get

$$T = 394 - 273 = \boxed{121 \text{ C}^\circ}$$

Thus, the correct answer is **B**.

23. To solve for the standard formation of  $\text{C}_3\text{H}_6\text{Br}_2$ , we can set up an equation for the standard enthalpy of the reaction.

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_{\text{prod}}^\circ - \sum \Delta H_{\text{react}}^\circ$$

Substituting the values given in the question, we get the following equation, where  $x = \Delta H_f^\circ(\text{C}_3\text{H}_6\text{Br}_2)$ .

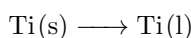
$$-122.5 = (x) - (20.4 + 30.9)$$

$$-122.5 + 20.4 + 30.9 = x$$

$$x = \boxed{-71.2 \frac{\text{kJ}}{\text{mol}}}$$

Thus, the correct answer is **A**.

24. The process here is the melting of titanium, as shown below,



At the melting point, the solid phase reaches equilibrium with liquid phase, which indicates  $\Delta G = 0$ . Then we can use the Gibbs Free energy equation for this question, which states the following.

$$\Delta G_{\text{melting}} = \Delta H_{\text{melting}} - T\Delta S_{\text{melting}}$$

$$0 = 14.15 \times 10^3 - (1668 + 273) \times (97.53 - S_{\text{solid}}^{\circ})$$

$$S_{\text{solid}}^{\circ} = 90.24 \text{ J/(mol K)}$$

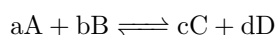
Thus, the answer is  $\boxed{B}$ .

25. We can use the stoichiometric coefficients to determine the relative rates of the reactants and products.

$$\frac{1.0 \text{ mol F}_2}{\text{L} \cdot \text{s}} \times \frac{2 \text{ mol ClF}_3}{3 \text{ mol F}_2} = \frac{0.67 \text{ M}}{\text{s}}$$

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

26. Our definition for equilibrium is that the forward rate of the reaction equals the reverse rate. Now to prove which of the remaining answer choices is correct, consider the following reaction.



From this, we can determine what  $k_f$  and  $k_r$  (the forward and reverse rates respectively).

$$\text{rate(f)} = k_f[A]^a[B]^b$$

$$\text{rate(r)} = k_r[C]^c[D]^d$$

Taking  $\text{rate(f)} = \text{rate(r)}$  at equilibrium state, we get

$$\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K$$

By law of mass action, the right hand side equals  $K$ . With the above derivation, we can use this information to solve for the reverse rate. Define  $F$  as the forward rate and  $R$  as the reverse rate. As stated previously, in equilibrium, we have that the forward rate equals the reverse rate.

$$F = R$$

$$k_f[A] = k_r(x)$$

where  $x$  is some combination of concentrations. Dividing by  $k_r$ , we get

$$x = \frac{k_f[A]}{k_r}$$

From the derivation, we know that  $k_f/k_r = K$ , or the equilibrium constant. Writing the equilibrium expression, we get

$$K = \frac{[C]}{[B][A]}$$

Substituting this into our expression, we get

$$x = \frac{[C]}{[B][A]} \cdot [A] = \frac{[C]}{[B]}$$

Finally, we substitute this into the expression for the reverse rate to get

$$R = k_r(x) = \frac{k_r[C]}{[B]}$$

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

27. This question is an application of the integrated rate law of the first order. We can write the linear dependence of a first-order reaction as follows.

$$\ln[A] = \ln[A_0] - kt$$

where the slope is  $-k$ , where  $k$  is the rate constant, and the  $y$ -intercept is  $\ln[A]_0$ . The equation describes a linear dependence with  $t$  vs  $\ln[A]$  with a negative slope. This matches the  $\boxed{\text{first order}}$  reaction, and thus, the answer is  $\boxed{B}$ .

**28.** We can immediately eliminate  $C$  as this is the definition of a homogeneous catalyst, not a catalyst in general. There are, to be specific, three types of catalysts labeled as homogeneous catalysts (same phase as reactants), heterogeneous catalysts (different phase than reactants), and enzymes (catalysts in living organisms).

We can also eliminate  $D$  since catalysis is defined as providing an *alternate* reaction mechanism with a lower activation energy, as opposed to proceeding by the same reaction mechanism.

Finally, we can also eliminate  $B$  because a chiral catalyst may produce one enantiomer over another one, which is the mirror image.

Thus,  $A$  must be the correct answer. This is because the catalyst reduces the activation energy of both the forward and backward activation energy. If the activation energy is reduced, then the rate of the forward and backward rate must increase in response.

**29.** Writing out the general equation for radioactive decay, which can be derived by using the integrated rate law of first order reaction, we have

$$A = A_0 \left( \frac{1}{2} \right)^{\frac{t}{t_{1/2}}}$$

where  $A_0$  is the initial amount,  $A$  is the current amount,  $t$  being the time elapsed, and  $t_{1/2}$  being the half-life, or how long it takes the compound to half in amount.

We are given that  $t_{1/2} = 1600$  y, and want to determine the time taken for 25% of the compound to disappear. If 25% disappears, then that would indicate that  $A = 0.75A_0$ , since 75% of the compound remains. Substituting this into the aforementioned equation, we can solve for  $t$ .

$$\begin{aligned} 0.75A_0 &= A_0 \left( \frac{1}{2} \right)^{\frac{t}{1600}} \\ 0.75 &= \left( \frac{1}{2} \right)^{\frac{t}{1600}} \\ \ln(0.75) &= \frac{t \ln(0.5)}{1600} \\ t &= \frac{1600 \ln(0.75)}{\ln(0.5)} = 664.06 \text{ y} \approx \boxed{660 \text{ y}} \end{aligned}$$

Thus, the correct answer is  $A$ .

**30.** For a fast first step in a reaction mechanism, we can use a pre-equilibrium approximation to solve for the rate. From the first step, which is at equilibrium, we have the following equation, with  $K$  being the equilibrium constant for the first elementary step.

$$K = \frac{[I_2][I^-]}{[I_3^-]}$$

For the second elementary step, which is the slow step, we can write the rate law for it, where  $k_1$  is the forward rate constant.

$$R = k_1[SO_3^{2-}][I_2]$$

Under the pretenses of the pre-equilibrium approximation, the production and consumption rate of the intermediate are equal. In this case,  $I_2$  is the intermediate, so we can solve for  $[I_2]$  in the first equation and substitute into the second one. Doing this, we get

$$\frac{K \cdot [I_3^-]}{[I^-]} = [I_2]$$

Substituting this into the second equation, we get the following expression.

$$R = \frac{K \cdot [I_3^-] \cdot k_1[SO_3^{2-}]}{[I^-]}$$

Removing the constants out of the rate law, and assigning them to an effective rate constant  $k$ , we get that the final answer is the expression below.

$$R = \frac{k \cdot [\text{I}_3^-][\text{SO}_3^{2-}]}{[\text{I}^-]}$$

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

**31.** We can use the law of mass action to solve this problem. Note that solid  $\text{Cu}(\text{OH})_2$  has an equilibrium activity of 1, and thus will not be represented in the equilibrium expression. Thus, we have the following expression.

$$K = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}][\text{OH}^-]^2}{[\text{NH}_3]^4}$$

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

**32.** Since HF is a weak acid, we need to write the RICE table associated with the reaction. Say  $C_0$  is the initial concentration of HF. Setting up the RICE table, we get

R	HF	+ H <sub>2</sub> O	$\rightleftharpoons$	F <sup>-</sup>	+ H <sub>3</sub> O <sup>+</sup>
I	$C_0$	-		0	0
C	$-x$	-		$+x$	$+x$
E	$C_0 - x$	-		$x$	$x$

Finally, we have one more piece of information due to the weak acid dissociation, and that is the change in concentration  $x$  is negligible with respect to  $C_0$ , or in mathematical terms,  $C_0 \gg x$ , as indicated by the very small  $K_a$  value. From the RICE table, we clearly see that  $\boxed{[\text{HF}] > [\text{F}^-]}$ . Thus, the correct answer is  $\boxed{C}$ .

**33.** First, we must write the dissolution reaction for  $\text{Ag}_2\text{CO}_4$  in order to write an expression for  $K_{\text{sp}}$ . The common ion effect is in effect here due to the presence of 0.050 M sodium oxalate  $\text{Na}_2\text{C}_2\text{O}_4$ , and thus each of the respective ions  $2\text{Na}^+$  and  $\text{C}_2\text{O}_4^{2-}$  have concentration of 0.050 M. Writing the RICE table, where  $S$  is the solubility of silver oxalate, we get

R	$\text{Ag}_2\text{CO}_4$	$\rightleftharpoons$	$2\text{Ag}^+$	+ $\text{C}_2\text{O}_4^{2-}$
I	-		0	0.05
C	-		$+2S$	$+S$
E	-		$2S$	$0.050 + S$

Writing our  $K_{\text{sp}}$  expression, we get

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{2-}] = (2S)^2(0.050 + S)$$

By our equilibrium approximation, we have that  $0.050 + S \approx 0.050$ , and substituting this, we get

$$3.5 \times 10^{-11} = (2S)^2(0.050)$$

$$S = \boxed{1.3 \times 10^{-5} \text{ M}}$$

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

Moreover, the  $S$  calculated is much smaller than 0.050, showing that our approximation is reasonable.

**34.** This problem can be solved using the Henderson-Hasselbalch equation, which states

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$$

From the problem, we know that  $\text{pH} = 4.15$  when 20.0 mL NaOH solution is added. Given that 50.0 mL of NaOH is needed to completely neutralize the acid, at the desired point, 20.0 mL of NaOH have been added, another 30.0 mL of NaOH is needed to neutralize the remained acid in the system.



Therefore, the ratio of the concentrations of reacted acid to un-reacted acid will be 20.0/30.0. This can then be used to determine the  $pK_a$ .

$$4.15 = pK_a + \log\left(\frac{20.0}{30.0}\right)$$

$$pK_a = \boxed{4.33}$$

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

**35.** The phrase indicating that the reaction mixture stops changing indicates that equilibrium has been reached. Note that all of the starting concentrations are 1.00 M, since all of the reactants are initially at 1.00 mole in a 1.00 L vessel.

If 79% of the  $H_2$  has reacted, that means the final concentration for  $H_2$  is 0.21 M, and the change in concentration is 0.79 M. Using this, we must write out our RICE table, as shown below.

R	$H_2$	+	$I_2$	$\rightleftharpoons$	$2 HI$
I	1.00		1.00		0
C	-0.79		-0.79		+2(0.79)
E	0.21		0.21		1.58

From the written reaction, we have the equilibrium concentrations, and the equilibrium expression written below.

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.58)^2}{(0.21)^2} = \boxed{56.6}$$

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

**36.** The critical observation here is that at the half equivalence point on the titration graph (or alternatively, the midpoint between the equivalence point and the origin) occurs when  $pH = pK_a$ . We can quickly derive this using the Henderson-Hasselbalch equation, which states

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Since we are titrating a triprotic acid with a strong base, the half equivalence point will denote when we have added enough moles of base to neutralize half of the moles of acid. However, upon consumption of the moles of weak acid, we have the production of the same amount of moles of its conjugate base. Thus, we have that

$$[A^-] = [HA]$$

Substituting this, we get

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log(1) = pK_a$$

In order to determine the equivalence points, we need to first determine where the equivalence points are located. Note that there are multiple equivalence points since it is a triprotic acid and has the ability to donate three hydrogens. Looking at the graph, the points where there is a slight shift upwards are indicative of a equivalence point, since that is where full neutralization takes place. This occurs when 10.0 mL, 20.0 mL, and 30.0 mL of NaOH have been added.

By the definition of half equivalence points, we need to take the midpoint between successive equivalence points in this case to get the respective volumes of 5.0 mL, 15.0 mL, and 25.0 mL of NaOH have been added. Finally, reading the graph, we see that the pH values that are closest at these points are  $\boxed{2.6, 5.0, 8.2}$ , or  $\boxed{A}$ .

**37.** Define  $\mathcal{O}(A)$  to be the oxidation state of element A. In order to have a stable compound, the sum of the oxidation numbers must equal 0. Thus, we have the following equation to solve for  $\mathcal{O}(\text{Sn})$ .

$$21\mathcal{O}(\text{Sn}) + 16\mathcal{O}(\text{Cl}) + 14\mathcal{O}(\text{O}) + 14\mathcal{O}(\text{H}) + 6\mathcal{O}(\text{O}) = 0$$

$$21\mathcal{O}(\text{Sn}) + 16(-1) + 14(-2) + 14(1) + 6(-2) = 0$$

$$21\mathcal{O}(\text{Sn}) - 16 - 28 + 14 - 12 = 0$$

$$21\mathcal{O}(\text{Sn}) - 44 + 2 = 0$$

$$21\mathcal{O}(\text{Sn}) = 42$$

$$\boxed{\mathcal{O}(\text{Sn}) = 2}$$

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

**38.** Recalling that an inert electrode only serves as an infinite receiver or giver (sink or source, in technical terms) of electrons throughout the reaction. The electrode itself does not react with any components of the reaction, including the solution and the substrate among others.

In order to facilitate electron transfer, an electrode or another solid conductor must be placed. If all the components of the half-reactions are aqueous, gaseous, or anything other than a solid, an inert electrode is required.

Looking at  $\boxed{\text{both I and II}}$ , we see that both of the reactions have no electrode component and therefore require an inert electrode to facilitate the flow of electrons in the electrochemical cell. Thus, the correct answer is  $\boxed{C}$ . Commonly used inert electrodes are graphite and nonreactive metals like gold, platinum.

**39.** This question requires using Faraday's law of electrolysis, which in the simplest terms, states that the mass of elements deposited at the end of an electrode via an electrochemical cell is directly proportional to the charge associated. First, the oxidation state of Cr must be determined. Let  $\mathcal{O}(n)$  denote the oxidation state of element  $n$ .

$$2\mathcal{O}(\text{K}) + 2\mathcal{O}(\text{Cr}) + 7\mathcal{O}(\text{O}) = 0$$

$$2(+1) + 2\mathcal{O}(\text{Cr}) + 7(-2) = 0$$

$$2 + 2\mathcal{O}(\text{Cr}) - 14 = 0$$

$$2\mathcal{O}(\text{Cr}) = 12$$

$$\mathcal{O}(\text{Cr}) = 6$$

Dimensional analysis can be then used here to convert from the mass of the deposited material to the time taken to accumulate that deposit.

$$1.00 \times 10^3 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{51.9961 \text{ g Cr}} \times \frac{6 \text{ mol } e^-}{1 \text{ mol Cr}} \times \frac{96500 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ A}}{200.0 \text{ A} \cdot \text{s}} \times \frac{1 \text{ hr}}{3600 \text{ s}} = \boxed{15.5 \text{ hr}}$$

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

**40.** The third half reaction is the sum of the first one and the second one. However, standard potential is an intensive property, which can't be applied with the Hess's Law. We need to convert the potential to Gibbs free energy using the equation below.

$$\Delta G^\circ = -nFE^\circ$$

Say the first reaction has Gibbs free energy  $\Delta G_1^\circ$  and say the second reaction has Gibbs free energy of  $\Delta G_2^\circ$ .

$$\Delta G_1^\circ = (-1) \times F \times (-0.41)$$

$$\Delta G_2^\circ = (-2) \times F \times (-0.91)$$

Further defining the third reaction having Gibbs free energy  $\Delta G_3^\circ$ , we have the following.

$$\Delta G_3^\circ = (-3) \times F \times (E_3^\circ)$$

From our initial statement, we now have this equation.

$$\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$$

$$(-1) \times F \times (-0.41) + (-2) \times F \times (-0.91) = (-3) \times F \times (E_3^\circ)$$

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

$$E_3^\circ = \boxed{-0.74 \text{ V}}$$

41. Using  $\Delta G$  to find the relationship between  $E_{\text{cell}}^{\circ}$  and  $K_{\text{eq}}$ , we have the following.

$$\Delta G = -nFE_{\text{cell}}^{\circ} = -RT \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = \frac{nFE_{\text{cell}}^{\circ}}{RT}$$

Substituting the constants and temperature into the above equation, we can get a more commonly used expression of the equation as follows.

$$\log_{10}(K_{\text{eq}}) = \frac{n \cdot E_{\text{cell}}^{\circ}}{0.0592 \text{ V}}$$

Note that we now have the logarithm with a base of 10 is used to replace the natural logarithm, and a coefficient of  $2.303 = \ln(10)$  is applied to get the constant 0.0592.

$$0.0592 = 2.303 \times \frac{8.314 \times 298}{96500}$$

You can definitely use the equation expressed by natural logarithm to get the same results. The equation with the constant 0.0592 is good for  $E$ -pH diagram based calculations.

To find the  $\Delta E^{\circ}$  for the total reaction, the first half-reaction must be reversed, while the second half-reaction will remain the same. Thus, we have

$$E_{\text{cell}}^{\circ} = (-0.16 \text{ V}) + (0.27 \text{ V}) = 0.11 \text{ V}$$

The quantity  $n$  will be the number of electrons transferred in the half reactions, which would be  $n = 1$  in this problem. Substituting, we have the following.

$$\log_{10}(K_{\text{eq}}) = \frac{1 \cdot 0.11 \text{ V}}{0.0592 \text{ V}}$$

$$\log_{10}(K_{\text{eq}}) = 1.86$$

$$K_{\text{eq}} = \boxed{73}$$

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

42. Since the reaction is not at equilibrium, we must use the Nernst's equation, which states the following.

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

We are given that  $E^{\circ} = 1.51 \text{ V}$ . At pH = 5.00,  $[\text{H}^+] = 1.0 \times 10^{-5} \text{ M}$ , while other ions are still in standard state, which are all 1.0 M. Substituting into the above equation, we get

$$E = 1.51 - \frac{8.314 \times 298}{5 \times 96500} \cdot \ln \left( \frac{1}{(1.0 \times 10^{-5})^8} \right) = 1.04 \text{ V}$$

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

43. The first value ( $n$ ) is the principal quantum number ( $n = 1, 2, 3 \dots$ ), and represents the shell where the valence electron is located. Since sulfur is in the third row of the periodic table, we have  $n = 3$ , then we can eliminate choice C.

The second value ( $l$ ) is the angular momentum quantum number, and represents the subshell ( $l = 0, 1, 2, \dots, (n-1)$ ), when  $l = 0$ , it is the s subshell, when  $l = 1$ , it is the p subshell, then d ( $l = 2$ ) and f ( $l = 3$ ) subshells. As the valence electrons of S is  $3s^2 3p^4$ , the valence electrons have a  $l$  value of 0 or 1, which further eliminates option A and D. Thus, the answer is the below pairing, or  $\boxed{B}$ .

$$\text{quantum numbers} \in \boxed{\left\{ 3, 1, -1, \frac{1}{2} \right\}}$$

The next value  $m_l$  is the magnetic quantum number ( $m_l = -l, \dots, +l$ ), and represents the orientation of orbital in each subshell. The last value is the spin quantum number  $m_s$ , which can only have two values,  $+1/2$  or  $-1/2$ .

44. The key insight for this question is observing when the largest jump in the successive ionization energies occurs, since this when all the valence electrons have been excited and left the outer shell. Since the biggest jump occurs from  $IE_4$  to  $IE_5$ , there must be 4 valence electrons in the desired element. The element in period 3 that has 4 valence electrons is  $\boxed{\text{Si}}$ . Thus, the answer is  $\boxed{B}$ .

45. Checking the location of Co in the periodic table, we can easily determine that the electron configuration of Co atom at ground state is  $[\text{Ar}]3d^74s^2$ , when it is ionized, the outermost electrons are removed first, thus the electron configuration of  $\text{Co}^{2+}$  at ground state is  $\boxed{[\text{Ar}]3d^7}$ , which is  $\boxed{D}$ .

46. The energy of light is proportional to its frequency, and inversely proportional to its wavelength, according to the equation below,

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

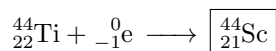
Thus,

$$\Delta E = hc \cdot \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = (6.626 \times 10^{-34}) \times (2.998 \times 10^8) \times \left( \frac{1}{485 \times 10^{-9}} - \frac{1}{540 \times 10^{-9}} \right) = \boxed{4.17 \times 10^{-20} \text{ J}}$$

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

47. The elements in the top right corner of the periodic table except those noble gases generally have larger electron affinity as they are small in size and high in nuclear charge. So among the four options, the element  $\boxed{\text{Cl}}$ , or  $\boxed{B}$  has the the highest electron affinity, releasing the most energy when an electron is added to it.

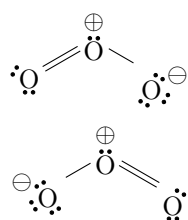
48. Recall that the definition of electron capture indicates that the parent element is the loss of one proton and no change in the atomic mass. With this description in mind, we have the following reaction.



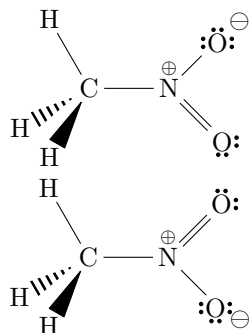
Thus, the correct answer is  $\boxed{C}$ .

49. In order to have the strongest C–O bond, the species must have the largest bond order. Drawing the Lewis structure for each of the species, we can easily figure out there is triple bond in CO, which is the strongest. The C–O bond order of B, C, D is 2, 2, 1, respectively. Thus, the species with the strongest C–O bond is  $\boxed{\text{CO}}$ , or  $\boxed{A}$ .

50. Ozone is the only polar molecule here as shown by the two resonances below, the central oxygen is positive, and the terminal oxygen with a single bond in each resonance is negative, which indicates a dipole moment bisecting the O–O–O angle. Thus, the correct answer is  $\boxed{\text{O}_3}$ , or  $\boxed{B}$ .



51. Drawing the resonance structures of  $\text{H}_3\text{C}-\text{NO}_2$ , we can figure out the two N–O bonds have the same length, thus A is incorrect, while  $\boxed{D}$  is correct as there are three electron domains around the central nitrogen, and therefore has  $\boxed{\text{trigonal planar geometry}}$ .



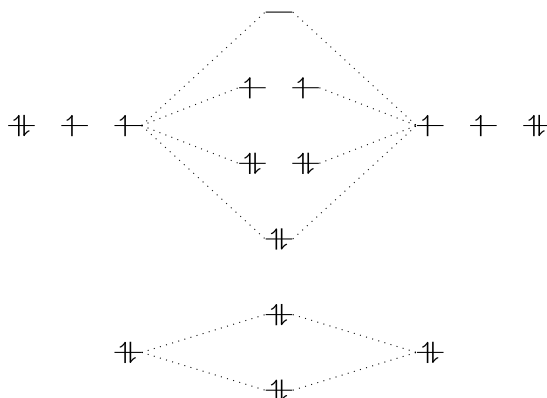
52. Recall the molecular orbital diagram of  $O_2$ , which has 6 bonding electrons and 2 **unpaired** anti-bonding electrons in the 2p subshell. superoxide ion,  $O_2^-$ , which has one more electron than  $O_2$ , should have one extra anti-bonding electron. The formula for bond order is as follows, where  $N_b$  is the number of electrons in bonding orbitals and  $N_a$  is the number of electrons in the anti-bonding orbitals.

$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

$$\text{Bond Order} = \frac{6 - 3}{2} = \frac{3}{2} = 1.5$$

Thus, the first statement is false since the bond order of the superoxide ion is 1.5, not 2.

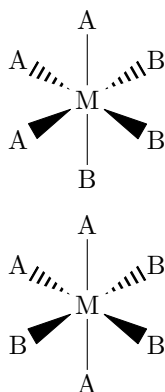
As for the second statement,  $O_2$  by itself has 2 unpaired electrons. However, with the superoxide ion introducing another electron, one of the initially unpaired electrons will now be paired. Thus, one unpaired electron remains and the second statement holds true.



Thus,  II only  is correct, and the correct answer is  B .

53. Per the Lewis structure of  $P_4$ , each phosphorus atom connects to three other phosphorus through a single bond, and carries one lone pair. The geometry of the molecule is a perfect tetrahedron. The answer choice that most closely resembles the most stable structure is  D .

54. For the octahedral coordination complex  $Co(NH_3)_3Cl_3$ , there are  2  geometric isomers available, the *-fac* and the *-mer* ones, respectively drawn below. Thus, the answer is  B .



55. The systematic name of the molecule in option C is 2-methyl-1-butene as we need the number the carbons on the main chain from left to right to minimize the position of the functional group, the  $C=C$  bond. Thus, the answer is  C .

56. The two molecules are *cis*-1,3-dichlorocyclopentane and *trans*-1,3-dichlorocyclopentane, respectively. So they are  geometric isomers , and the correct answer is  C . Moreover, as they are stereoisomers but not enantiomers (mirror images), they are also called diastereomers.

57. In organic chemistry, amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines possess a characteristic ammonia smell, liquid amines have a distinctive "fishy" and unpleasant odor. Thus, A is correct.

An amine with the formula  $C_4H_{11}N$  can be primary ( $RNH_2$ ), secondary ( $RNHR'$ ), or tertiary ( $RNR'R''$ ). Primary and secondary amines can make hydrogen bonds with water through the  $N-H \cdots O$  interaction, which can make its water solubility higher than 10 g/L, so D is incorrect.

Amines are colorless, which won't absorb any light in the visible range, thus, choice C, absorption of light with  $\lambda > 450$  nm, is incorrect. Strictly speaking, amines are IR active, the vibrations of chemical bonds can absorb the IR light, which has a  $\lambda > 450$  nm. So a better phrasing might be absorption of **visible** light with  $\lambda > 450$  nm.

Choice B, boiling point greater than 100 °C is a comparison of the boiling point with that of water. Though primary and secondary amines can make hydrogen bonds among the molecules, which makes their boiling points higher than the alkanes with similar molar masses. However, the hydrogen bonds in amines are weaker than that in water, thus, it is less likely for an amine with four carbons to have a boiling point higher than 100 °C, choice B is therefore eliminated.

58. Methyl propanoate,  $CH_3CH_2COOCH_3$  is an ester, which is typically synthesized by reacting propanoic acid,  $CH_3CH_2COOH$  with methanol,  $CH_3OH$  under the presence of acid as catalyst. Thus, D is the correct answer.

59. The chair conformation, or B is the most stable conformation for cyclohexane, as it does not have any steric hindrance or steric repulsion between the hydrogen bonds.

60. The three components of DNA are as follows.

- The nitrogen-containing base is either a pyrimidine base (one-ring formation) or a purine base (two-ring formation). Therefore, B is incorrect.
- The deoxyribose sugar is a ring of 5 carbons that bonded to the nitrogen-containing base to form a nucleoside.
- The phosphate group is the third component of DNA, which binds to the nucleoside to form a DNA nucleotide. Therefore, C is incorrect.
- Both the nitrogenous base and five-carbon sugar has many hydrogen atoms in the structure. Thus, A is incorrect.

Thus, the only element not present in DNA is S, or D. S is a common element in peptide and proteins.