

Annotated Solution

2018 USNCO National Exam Part I

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Solutions

1. The only two product from the reaction are water and metallic manganese. Thus, the sum of the mass of oxygen in water and manganese must equal to the total mass.

$$m_{\text{O}} = 0.235 \times \frac{16.0 \text{ g/mol}}{18.0 \text{ g/mol}} = 0.209 \text{ g}$$

$$m_{\text{Mn}} = 0.688 \text{ g} - 0.209 \text{ g} = 0.479 \text{ g}$$

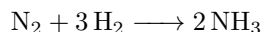
$$n_{\text{O}} = \frac{0.209 \text{ g}}{16.0 \text{ g/mol}} = 1.31 \times 10^{-2} \text{ mol}$$

$$n_{\text{Mn}} = \frac{0.479 \text{ g}}{54.9 \text{ g/mol}} = 8.72 \times 10^{-3} \text{ mol}$$

$$\text{Mn} : \text{O} = 2 : 3$$

Therefore, the answer is $\boxed{\text{Mn}_2\text{O}_3}$, or \boxed{B} .

2. The compound that has the smallest molar mass will have the most number of molecules since the mass of the sample is the same. Therefore, the answer is $\boxed{\text{O}_3}$, or \boxed{B} .
3. Let's first balance the equation:



From the stoichiometric ratio, we can see that the volume of hydrogen gas need to be three times of that of nitrogen as the volume is proportional to the mole of gas under the same condition. Therefore, the answer is $\boxed{15.0 \text{ L}}$, or \boxed{C} .

4. For convenience, the reaction will be also mentioned here:



We now need to perform stoichiometric manipulations.
Let's begin by finding the moles of produced H_3PO_4 :

$$n(\text{H}_3\text{PO}_4) = \frac{1.00 \times 10^6 \text{ g}}{98.0 \text{ g/mol}} = 10.2 \text{ kmol}$$

Using the balanced equation that is given in the problem, we proceed to find the necessary number of moles of $\text{Ca}_3(\text{PO}_4)_2$ and SiO_2 that react in 100% yield to give 10.2 kmol of H_3PO_4 :

$$n(\text{Ca}_3(\text{PO}_4)_2) = \frac{1}{2} \times 10.2 = 5.10 \text{ kmol}$$

$$n(\text{SiO}_2) = \frac{3}{2} \times 10.2 = 15.3 \text{ kmol}$$

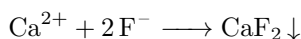
Now we can find the necessary masses of each of these compounds:

$$\begin{aligned} m(\text{Ca}_3(\text{PO}_4)_2) &= n(\text{Ca}_3(\text{PO}_4)_2) \times M(\text{Ca}_3(\text{PO}_4)_2) \\ &= 1580 \text{ kg} \end{aligned}$$

$$\begin{aligned} m(\text{SiO}_2) &= n(\text{SiO}_2) \times M(\text{SiO}_2) \\ &= 918 \text{ kg} \end{aligned}$$

Now, remember that we are asked to take equal masses of $\text{Ca}_3(\text{PO}_4)_2$ and SiO_2 . Notice that the necessary masses that we found earlier satisfy: $m(\text{Ca}_3(\text{PO}_4)_2) > m(\text{SiO}_2)$. Thus, if we take 1580 kg of both $\text{Ca}_3(\text{PO}_4)_2$ and SiO_2 we will have enough material to produce 10^3 kg of H_3PO_4 and we will have some excess of SiO_2 left. However, if we take 918 kg of both $\text{Ca}_3(\text{PO}_4)_2$ and SiO_2 , we won't have enough $\text{Ca}_3(\text{PO}_4)_2$ to produce 10^3 kg of H_3PO_4 (remember that we need at least 1580 kg of $\text{Ca}_3(\text{PO}_4)_2$). Thus, the answer is \boxed{D} .

5. When solutions that contain Ca^{2+} and F^- are mixed, a precipitate of CaF_2 is observed:



Let's calculate the initial number of moles that are mixed:

$$n(\text{Ca}^{2+}) = 30.0 \text{ mL} \times 0.30 \text{ M} = 9.0 \text{ mmol} \qquad n(\text{F}^-) = 15.0 \text{ mL} \times 0.60 \text{ M} = 9.0 \text{ mmol}$$

Thus, after all the 9.0 mmol of F^- react, we will be left with 4.5 mmol of Ca^{2+} .

The total volume of the mixed solution is $30.0 + 15.0 = 45.0$ mL.

Thus, the concentration of the Ca^{2+} ions is:

$$[\text{Ca}^{2+}] = \frac{4.5}{45.0} = 0.10 \text{ M}$$

The correct answer is \boxed{A} .

6. The molecular formula, $\text{Na}_2\text{S}_x\text{O}_y$ has two unknowns, and the molecular mass of the salt cannot be calculated. The simplest method to find 'x' is by trial and error using the answer choices as both x and y are supposed to be integers.

If $x = 4$, the possible anion is $[\text{S}_4\text{O}_6]^{2-}$ which is the product when thiosulfate ($\text{S}_2\text{O}_3^{2-}$) is oxidized, giving us the formula $\text{Na}_2\text{S}_4\text{O}_6$. Calculating the molecular mass, we get:

$$\left(2 \times \frac{23.0 \text{ g Na}}{1 \text{ mole Na}}\right) + \left(4 \times \frac{32.0 \text{ g S}}{1 \text{ mole S}}\right) + \left(6 \times \frac{16.0 \text{ g O}}{1 \text{ mole O}}\right) = 270.0 \frac{\text{g}}{\text{mol}}$$

$$\%S = 4 \left(\frac{32.0}{270.0}\right) \times 100 = 47.5\%$$

The given value for %S of the unknown in the problem is in agreement with our calculated value. Hence, we can say that the molecular formula of our unknown salt, $\text{Na}_2\text{S}_x\text{O}_y$ is $\text{Na}_2\text{S}_4\text{O}_6$. Therefore, the value of x is 4, and the correct answer is \boxed{D} .

A more general way is to use the mass percent of S:

$$\text{S}\% = \frac{32.0x}{23.0 \times 2 + 32.0x + 16.0y} = 47.5\%$$

Then, try $x = 1, 2, 3$, or 4, the x value which can give an integral y is the correct answer.

7. Diamagnetism implies that the substance has NO unpaired electrons, and is not attracted by a magnetic field.

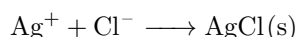
- In $\text{K}_2[\text{NO}(\text{SO}_3)_2]$, the cation, K^+ has an octet and no unpaired electron, so does the SO_3^{2-} . However, the anion $[\text{NO}(\text{SO}_3)_2]^{2-}$ has a nitrogen in the +4 oxidation state, which translates to a configuration of $1s^2 2s^1$ with an unpaired electron, ruling out choice **A**.
- For the ionic compound $\text{Ce}_2(\text{SO}_4)_3$, the cation Ce^{3+} has a configuration of $[\text{Xe}]4f^1$. The unpaired f^1 electron results in the compound being paramagnetic, ruling out choice **C**.
- Both $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{Hg}[\text{Co}(\text{SCN})_4]$ are coordinate complexes. The transition metals Fe and Co are both in the +2 oxidation state. The Fe^{2+} has a configuration of d^6 , while the Co^{2+} has a configuration of d^7 . The strong CN^- ligands cause a splitting of the d-orbitals in Fe^{2+} , with the three lower energy d-orbitals being completely full with 6 electrons, making it diamagnetic, the correct choice is **B**. The cobalt ion has odd number of electrons, making it paramagnetic, ruling out choice **D**.

Hence, the correct answer is \boxed{B} .

You may need to further read "Crystal Field Theory" for more information about the split of d orbitals in octahedral complexes.

8. An indicator acts as a chemical detector, and is used to determine the end point of a reaction. Acids and bases are typically colorless solutions, and hence acid-base reactions require the use of indicators, to indicate the change in pH of the solution.

- Choices **C** and **D** can be eliminated as they are acid-base reactions requiring the addition of indicators.
- The titration reaction for the determination of chloride ions (choice **B**) is as follows:

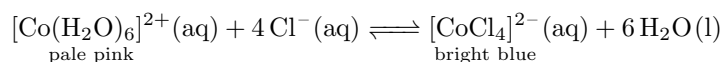


The reaction is complete when all the chloride ions have precipitated. Any additional Ag^+ ions react with an added indicator CrO_4^{2-} to form a reddish-brown precipitate which is different from the white $\text{AgCl}(s)$, and the end point can be determined. Hence, choice **B** also can be eliminated as it requires added indicator.

- By elimination, we can conclude that choice **A** is the correct answer. The reaction is a redox titration accompanied by a color change from deep purple of the permanganate ion, which gets reduced to colorless Mn^{2+} . The permanganate ion acts as its own indicator to determine the end point.

Hence, the correct answer is \boxed{A} .

9. A divalent metal ion means a metal ion with oxidation state of +2. However, this isn't a useful clue because all metal ions in the choices are all divalent. So, the only clue left is the colour of the solution before and after the addition of concentrated HCl. Upon its reaction, the only metal ion that undergoes such colour changes is Co^{2+} ion. The actual reaction that happens is as follows:

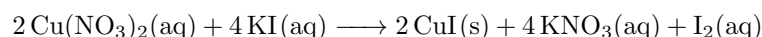


Hence, the answer is $\boxed{\text{Co}^{2+}}$ or \boxed{C} .

10. Concentrated nitric acid acts as a strong oxidizing agent and facilitates the oxidation of Copper and Nickel. The reaction of copper with nitric acid is a redox reaction where copper gets oxidized to the +2 state and the nitrogen in the acid is reduced to +4 or +2 from +5. The oxidation number of N in the product NO_x depends on the acid concentration. Since 8 M HNO_3 is concentrated, the reaction proceeds as follows with a reddish brown gas $\text{NO}_2(g)$ produced:



In the presence of dilute excess KI, the $\text{Cu}(\text{NO}_3)_2$ gets reduced by another redox reaction. The copper ion is reduced to Cu^+ and not Cu because CuI is a precipitate, similar to AgI . $\text{I}_2(\text{aq})$ is actually existed mainly in the form of $\text{I}_3^-(\text{aq})$ with the presence of excess $\text{I}^-(\text{aq})$.



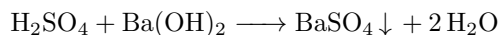
Let us now look at the reaction of HNO_3 from the perspective of Ni.



Choice **B** is incorrect, as $\text{NiI}_2(\text{aq})$ is soluble. The only choice with $\text{CuI}(s)$ as a product is **C**. Hence, the answer is \boxed{C} .

Readers may practice writing the net ionic equations of the reactions above.

11. The reaction between an aqueous solution of H_2SO_4 and an aqueous solution of $\text{Ba}(\text{OH})_2$:



The conductivity of the solution is dependent on the presence of ions in the solution. During the titration the number of ions in the solution decreases, because the H^+ and HSO_4^- ions react to produce the solid BaSO_4 and neutral liquid water.

The conductivity continues to decrease until the equivalence point where all the original H_2SO_4 has reacted. From this point, adding more $\text{Ba}(\text{OH})_2$ produces Ba^{2+} and hydroxide ions that increase the conductivity. Therefore, the answer is \boxed{D} .

12. While this problem can be approached by several problem-solving strategies, the solution below will use the process of elimination in order to explain why each answer is either right or wrong.

- Choice **A** is wrong. Water should never be added to a solution of concentrated H_2SO_4 . This is because the dissolution of concentrated sulfuric acid releases a lot of heat which may severely heat the reaction vessel and cause the solution to squirt. Rather, H_2SO_4 is usually added dropwise to an aqueous solution. The diffusion of a small concentration of acidic protons is less significant in this way, thus reducing the chance of dangerous heat accumulation.
- Choice **B** is wrong from the same reason as choice **A**.
- Choice **C** is the answer here. Taking a mass of 98.1 g of the concentrated H_2SO_4 solution will result in the final solution in a safe way.
- Choice **D** is wrong, dilution of concentration H_2SO_4 in the volumetric flask directly is prohibited as the volume of the flask will be largely affected by the heat released from the dilution process.

Thus, the answer is \boxed{C} .

Readers can further confirm the molarity of H_2SO_4 prepared using the method in **C** by assuming the molarity of the original concentrated H_2SO_4 is 18.4 M.

13. Taking into account the relatively high density of the substance and that is not significantly compressible, one can easily eliminate the possibility of a gas. However, whether the substance is a solid or a liquid cannot be determined. The density is more consistent with that for liquids, though some liquids such as mercury is really heavy. However, some light solids such as alkali metals, alkaline earth metals may also have a low density like this. The answer is \boxed{D} .
14. The intermolecular forces (IMFs) in molecules can help us predict the trends in boiling points. The stronger the IMFs in a molecule, the lower will be its vapor pressure and the higher the boiling point.

Let us now look into the IMFs of CCl_4 and CHCl_3 . Both CCl_4 and CHCl_3 have a tetrahedral geometry. The CCl_4 molecule is non-polar while the CHCl_3 is a polar molecule. As a result, the CCl_4 molecule has only London dispersion while the CHCl_3 has both London dispersion as well as dipole-dipole interactions. Based on these concepts, we expect the CHCl_3 molecule to have a higher boiling point. However, the data in the problem suggests otherwise, CCl_4 with 77°C and CHCl_3 with 61°C . This is best explained by suggesting that the London dispersion forces in CCl_4 is stronger than the combined London dispersion and dipole-dipole forces in CHCl_3 , considering that CCl_4 has a larger molar mass and the polarity of CHCl_3 is relatively small. London dispersion forces was the deciding factor in explaining the boiling point trend between the two molecules.

Hence, the correct answer is \boxed{C} .

15. Hydrogen bond is a type of special interaction between the positive charged H in a molecule with a O–H, N–H or F–H covalent bond and another molecule with a small but electronegative atom such as O, N or F.

Bonds A and C are clearly covalent bonds between non-metals, so that rules out choices **A**, **C** and **D**. By elimination, **B** is the correct answer, and we also see that it is between positive H in one molecule and a O–H bond in another molecule.

Hence, the correct answer is \boxed{B} .

16. We can think that the phase diagram is composed of three lines: a line between solid and liquid, a line between liquid and vapor, and a line between solid and vapor.

The critical point is the point where all three lines intersect, which means that the three phases of the compound are in co-equilibrium. This also means that the critical point is on all of the three line.

Therefore, combined with the information that ammonia melts at 195.42 K and 1 bar, we can calculate the slope of the line that's between solid and liquid. The result shows that this line has a positive slope. Thus, solid ammonia is denser than liquid ammonia as higher pressure compresses liquid ammonia to solid at a constant temperature, and \boxed{A} is correct. (Try doing the same analysis for water, which has a higher density than ice.)

Please sketch the phase diagram to simplify your analysis above.

17. As long as some liquid is in the system, the vapor pressure of that liquid only depends on temperature. Their relationship is given by the equation:

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

Therefore, we need to check if there are enough acetone to maintain its saturated vapor pressure at the new volume.

$$n = \frac{PV}{RT} = \frac{30.7 \text{ kPa} \times 4.00 \text{ L}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}} = 0.0496 \text{ mol} < 0.100 \text{ mol}$$

Thus, the vapor pressure of acetone remains the same.

Because the question asks for the total pressure in the system, we need to combine the vapor pressure of acetone with the pressure of argon gas under the new volume.

$$P_1 V_1 = P_2 V_2$$

$$P_2(\text{argon}) = \frac{1.00}{4} = 0.250 \text{ bar}$$

$$P_{\text{tot}} = 0.250 \text{ bar} + 0.307 \text{ bar} = \boxed{0.557 \text{ bar}}$$

Answer is \boxed{C} .

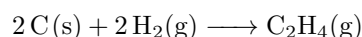
18.
 - Each atom on the vertices of the cubic unit cell contributes $\frac{1}{8}$ atoms to the unit cell.
 - Each atom on the faces of the cubic unit cell contributes $\frac{1}{2}$ atoms to the unit cell.
 - Each atom insides of the cubic unit cell contributes 1 atom to the unit cell.

Thus, we have:

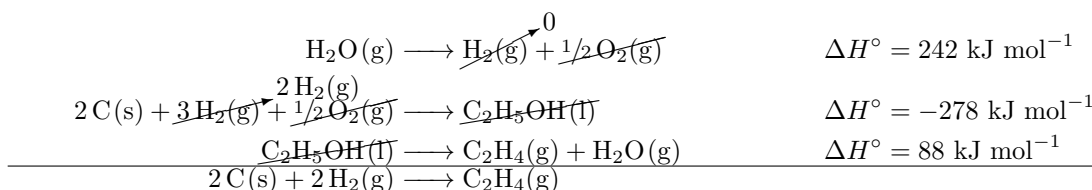
$8 \times 1 = 8$ oxygen atoms and $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ cerium atoms. The formula is then $\boxed{\text{CeO}_2}$ and the answer is \boxed{D} .

19. Because the reaction is endothermic, meaning it absorbs heat, the temperature of the system will decrease. Absorbing heat increases the internal energy of the reactants. Therefore, answer \boxed{C} is correct.

20. The reaction for the formation of C_2H_4 is given below:



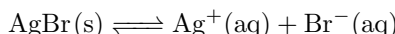
ΔH_f° for $\text{C}_2\text{H}_4(\text{g})$ needs to be calculated using the data given. Using Hess's Law, we can obtain the reaction for the formation of $\text{C}_2\text{H}_4(\text{g})$ by adding the three equations below:



Adding the values of ΔH° , we get the value of ΔH° for formation of C_2H_4 , which is 52 kJ/mol.

Hence, the correct answer is \boxed{B} .

21. Since the equilibrium constant K_{sp} for the dissolution of the solid AgBr(s) at two different temperatures is given, we can use the Van't Hoff equation to solve for ΔH° of the reaction



Substituting in the K values and their corresponding temperatures in Kelvin,

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{6.5 \times 10^{-12}}{5.0 \times 10^{-13}}\right) = \frac{-\Delta H^\circ}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

Solving for ΔH° , we get 82000 J mol^{-1} or 82 kJ mol^{-1} .

Here is the tricky part, the question gives you data to solve for $\Delta H_{\text{dissolution}}^\circ$ (which is ΔH° above) using the Van't Hoff equation, but is asking for the value of $\Delta H_{\text{precipitation}}^\circ$. Precipitation of AgBr(s) is the reverse reaction of the dissolution of AgBr(s) , hence the sign of ΔH° needs to be flipped.

$$\Delta H_{\text{precipitation}} = -\Delta H_{\text{dissolution}} = -\Delta H^\circ = -82 \text{ kJ.}$$

Hence, we can conclude that the answer is **A**.

22. This is a calorimetry question.

- We are starting with 1 mol of $\text{C}_6\text{H}_6(\text{s})$ at the melting point, 5°C .
- The 20 kJ of energy added will first be used to change the phase of C_6H_6 from solid to liquid, ΔH_{fusion} .
- For $\text{C}_6\text{H}_6(\text{s})$, $\Delta H_{\text{fusion}} = 9.9 \text{ kJ/mol}$, which results in $(20.0 - 9.9) = 10.1 \text{ kJ/mol}$ remaining.
- The remaining energy will be utilized in raising the temperature of the liquid. The temperature to which it is raised could be calculated using the $q = C_m \Delta T$ where C_m is the molar heat capacity of $\text{C}_6\text{H}_6(\text{l})$ and ΔT is the change in temperature, and $\Delta T = T_f - T_i$ where T_f and T_i are final and initial temperatures respectively.

$$10.1 \times 10^3 \text{ J} = 1 \text{ mol} \times 135 \frac{\text{J}}{\text{mol}} \times \Delta T$$

$$\text{Solving for } \Delta T, \text{ we get } \Delta T = 74.8^\circ\text{C}$$

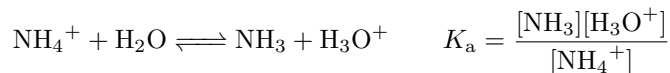
$$74.8^\circ\text{C} = T_f - 5^\circ\text{C}$$

$$T_f = 79.5^\circ\text{C}$$

$T_f = 79.5^\circ\text{C}$ which is $< 80^\circ\text{C}$, the boiling point of $\text{C}_6\text{H}_6(\text{l})$. This implies that C_6H_6 exists only in the **liquid** phase when 20 kJ of energy is supplied to 1 mole of $\text{C}_6\text{H}_6(\text{s})$.

Hence, we can conclude that the answer is **B**.

23. The term K_a suggests acid hydrolysis of NH_4^+



We know that

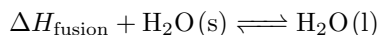
$$\Delta G^\circ = -RT \ln(K_a) \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Combining the two equations we get the van't Hoff equation: $\ln(K_a) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$

- The graph shows that $\ln(K_a)$ decreases with $\frac{1}{T}$. This indicates that K_a increases with temperature, T . Based on the K_a expression for the acid hydrolysis reaction above as K_a increases, more $[\text{H}_3\text{O}^+]$ is formed. We know that $\text{pH} = -\log[\text{H}_3\text{O}^+]$ which implies as more $[\text{H}_3\text{O}^+]$ is formed, pH value decreases. So **I** is **incorrect**, we can eliminate choices **A** and **C**.
- The graph also shows the y -intercept (which is $\frac{\Delta S^\circ}{R}$ from our equation) to be a negative value. $\frac{\Delta S^\circ}{R} = -0.215$ telling us that **II** is also **incorrect**.

Hence, we can conclude that the answer is **D**.

24. Method 1: The heat of fusion of ice is an endothermic process.



We can use the Van't Hoff equation to help answer the question. Setting ΔH_{fusion} as ΔH_{273} and ΔH_{263} for the two different temperatures we get:

$$\ln(K_2) = \frac{-\Delta H_{273}}{R} \left(\frac{1}{273} \right) + \text{constant}$$

$$\ln(K_1) = \frac{-\Delta H_{263}}{R} \left(\frac{1}{263} \right) + \text{constant}$$

An increase in temperature from 263 K to 273 K will favor the forward reaction, and therefore the $\Delta H_{263} < \Delta H_{273}$.

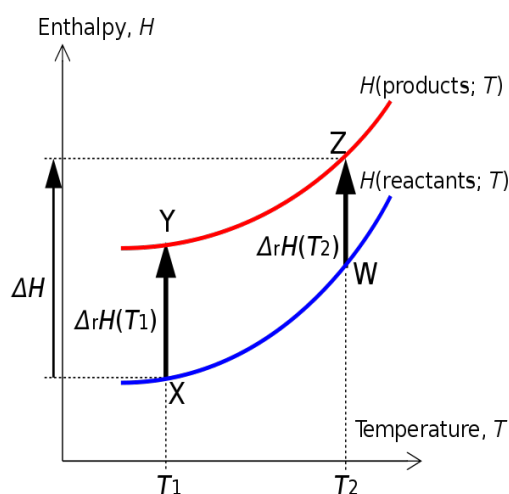
Hence, the correct choice is **A**.

Method 2: The problem can also be solved using the Kirchoff's Law, which is based on Hess's Law here, which states that

$$\begin{aligned} \Delta H_{\text{rxn}}(T_2) &= \Delta H_{\text{rxn}}(T_1) + \Delta C_p \times (T_2 - T_1) \\ \Delta H_{\text{rxn}}(273) &= \Delta H_{\text{rxn}}(263) + (76 - 37) \times (273 - 263) \\ \Delta H_{\text{rxn}}(273) &= \Delta H_{\text{rxn}}(263) + 390 \\ \Delta H_{\text{rxn}}(273) &> \Delta H_{\text{rxn}}(263) \end{aligned}$$

Hence, again the correct choice is **A**.

Sketching the cycle of the four processes with the Hess's Law applied is helpful to understand the work above. You may refer to the image below:



Source: Wikipedia

25. Don't get tricked by the existence of the chemical equation given in the question! It has nothing to do with what we are supposed to find since the overall reaction is not necessary to be an elementary one. Do bear in mind that the unit of rate must always be either M/s or M/min or M/hr or M/yr as long as it is concentration per unit time. Therefore, we just need to work out the units to determine the overall order of reaction.

$$\begin{aligned} \text{Rate} &= k[\text{A}]^n \\ \text{M s}^{-1} &= \text{M}^{-1}\text{s}^{-1} \cdot \text{M}^n \\ \text{M}^n &= \frac{\text{M s}^{-1}}{\text{M}^{-1}\text{s}^{-1}} = \text{M}^{1-(-1)} \cdot \text{s}^{-1-(-1)} \\ &= \text{M}^2 \\ n &= 2 \end{aligned}$$

Hence, we could conclude that the overall order of the reaction is $\boxed{2}$ or \boxed{C} .

26. Let's take a look at the first two rows in the table. Between these rows, [A] is doubled while [B] remains unchanged. Thus, we can determine the order of the reaction with respect to A. Since the total rate of the reaction is twice as much in the second row than in the first, the order with respect to A is 1. Applying the same procedure on the first and third rows (where [A] remains constant) we can deduce that the order with respect to B is 2. Thus, the correct rate law is given in choice \boxed{D} .

27. Radioactive decay follows first order kinetic laws. Thus, we can write:

$$\ln\left(\frac{A_t}{A_0}\right) = -kt$$

Where A_t and A_0 are the activities of ^{210}Po at time t and 0 respectively. We also know that $A_t = 0.15A_0$ and that for first order reactions $k = \frac{\ln 2}{t_{1/2}}$ where $t_{1/2}$ is the half-life time. Let's use this equation in order to find t while noticing the units:

$$\ln\left(\frac{0.15A_0}{A_0}\right) = -\left(\frac{\ln 2}{138 \text{ d}}\right) t$$

We then get that $t = 377 \text{ d}$. The correct answer is \boxed{D} .

28. This is a very tricky question. A linear relationship between $\ln[A]$ and time indeed indicates a first order reaction, and in this question, the concentration of the two reactants are the same, which means that this is not a pseudo first-order reaction. Instead, either A or B need to be zeroth order in the rate law, and the other reactant needs to be first order. The problem is that we can not be sure about which reactant is first order. This is because the two reactants have the same initial concentration and react in a ratio of one to one, which means that the concentration of A and B are the same through out the reaction! So if we were to plot $\ln([B])$ over time, we would get the exact same graph! Thus, we can not be sure about which reactant is first order. The answer is \boxed{D} . In a typical pseudo analysis, $[B] \gg [A]$, then We can assume [B] doesn't change with time when A is consumed, so rate = $k[A]^a[B]^b = k'[A]^a$, where $k' = k[B]^b$

29. Because the first equilibrium is faster than the following reactions, we can assume that the equilibrium is always established. Thus, we have the forward rate equals to the reverse rate for the first step:

Forward rate = Reverse rate

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2$$

Substitute this result into the second step, which is the rate-determining step, we have:

$$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2] = \frac{k_1 k_2}{k_{-1}}[\text{NO}]^2[\text{H}_2]$$

This is consistent with option \boxed{B} .

Note that the third reaction is fast and thus does not contribute much to the overall rate law.

30.
 - By reading the graph, we find that the reaction is exothermic because compared with the reactant, the product has a lower enthalpy. Thus, statement **I** is **incorrect**.
 - The activation energy is the difference in enthalpy between the reactant and the transition state. In this case, the activation energy would be

$$40 \text{ kJ} \cdot \text{mol}^{-1} - 18 \text{ kJ} \cdot \text{mol}^{-1} = 22 \text{ kJ} \cdot \text{mol}^{-1}$$

Thus, statement **II** is **incorrect**.

Therefore, the answer is \boxed{D} .

31. By definition, we have

$$K_{\text{sp}} = [\text{OH}^-]^2 \times [\text{Co}^{2+}] = 5.9 \times 10^{-15}$$

Suppose the concentration of cobalt ions is x ,

$$(2x)^2 \times x = 5.9 \times 10^{-15}$$

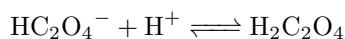
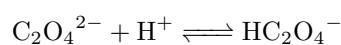
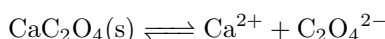
$$x = 1.14 \times 10^{-5}$$

$$[\text{OH}^-] = 2x = 2.28 \times 10^{-5} \text{ M}$$

$$\text{pH} = 14 + \log [\text{OH}^-] = \boxed{9.36}$$

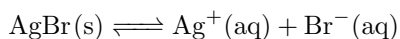
The answer is therefore \boxed{C} .

32. We know that $\text{C}_2\text{O}_4^{2-}$ is the conjugate base of a weak acid, which means that it's somewhat basic. So if the solid CaC_2O_4 is in an acidic solution, it can be better dissolved due to two new equilibriums:

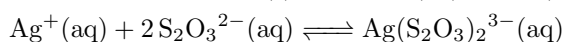


Therefore, we want to pick the answer choice that has the most acidic solution. In this case, the answer would be $\boxed{\text{HCl}}$, or \boxed{D} .

33. There are two equilibriums involved in this question:

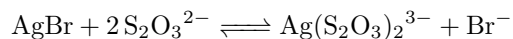


$$K_{\text{sp}} = 5.4 \times 10^{-13}$$



$$K_{\text{f}} = 2.8 \times 10^{13}$$

Let's simplify the calculation by combining the two equilibriums together:



$$K = K_{\text{sp}} \times K_{\text{f}}$$

$$\frac{[\text{Br}^-][\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{S}_2\text{O}_3^{2-}]^2} = K$$

Suppose that x mol of AgBr dissolved.

$$\frac{x^2}{(0.200 - 2x)^2} = K = 15$$

$$\frac{x}{0.200 - 2x} = \sqrt{K} = 3.9$$

After solving the equation, we find that $x = \boxed{0.089}$, or \boxed{A} .

34. Apply the Henderson-Hasselbalch equation (The mole ratio is the same as the concentration ratio since the two species are in the same solution):

$$\begin{aligned} \text{pH} &= \text{p}K_{\text{a}} + \log \frac{[\text{F}^-]}{[\text{HF}]} \\ &= -\log(6.8 \times 10^{-4}) + \log \left(\frac{0.23 \text{ M} \times 0.1250 \text{ L}}{0.15 \text{ M} \times 0.1000 \text{ L}} \right) \\ &= \boxed{3.45} \end{aligned}$$

The answer is therefore \boxed{D} .

35. Let's consider the following two equations:

$$\Delta G^\circ = -RT \ln(K_{\text{eq}})$$

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

From these two equations we can get another equation which relates $\ln(K_{\text{eq}})$ to ΔH° and ΔS° :

$$\ln(K_{\text{eq}}) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

Thus, since a graph of $\ln(K_{\text{eq}})$ vs. $1/T$ is linear and has a positive slope, ΔH° should be negative. However, we don't know about the intercept of this graph with the y -axis so we can't reach any conclusion about ΔS° . The correct answer is A

36. We shall use the ICE table for this equilibrium problem.

| | | | | | |
|---|------------------------|---|------------------------|----------------------|------------------------|
| | $\text{H}_2(\text{g})$ | + | $\text{I}_2(\text{g})$ | \rightleftharpoons | $2\text{HI}(\text{g})$ |
| I | 0.0500 | | 0.0500 | | 0 |
| C | $-x$ | | $-x$ | | $+2x$ |
| E | $0.0500-x$ | | $0.0500-x$ | | $+2x$ |

However, we are given K_p and not K_c . So, let's figure out what is the value of K_c using the formula below:

$$K_p = K_c(RT)^{\Delta n}$$

where Δn = the difference of stoichiometric coefficients of gas-phase species in the equation
or $\Delta n = n_{\text{products(g)}} - n_{\text{reactants(g)}}$
 R = ideal gas law constant
 T = temperature in Kelvin

Since $\Delta n = 2 - 2 = 0$, $K_p = K_c = 50.4$.

With that, we can proceed to solve the problem which is to deduce the number of moles of HI at equilibrium.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$50.4 = \frac{\left(\frac{2x}{3.00}\right)^2}{\left(\frac{0.0500-x}{3.00}\right)\left(\frac{0.0500-x}{3.00}\right)}$$

$$\sqrt{50.4} = \frac{2x}{0.0500 - x}$$

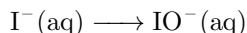
$$x = 0.0390 \text{ mol}$$

Do remind yourself that the number of moles of HI at equilibrium is $2x$. So, there are $2 \times 0.0390 =$ 0.0780 moles of HI at equilibrium. Hence, the answer is D.

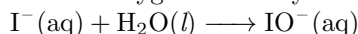
37. (Do take note that the reaction that occurs is in BASIC solution.)

Let's start by constructing the half-equation for oxidation reaction.

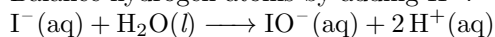
(a) Balance the number of moles of I atoms:



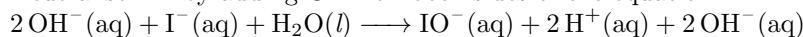
(b) Balance oxygen atoms by adding H_2O :



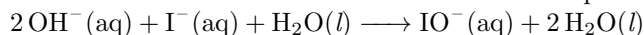
(c) Balance hydrogen atoms by adding H^+ :



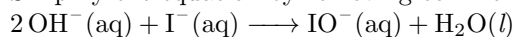
(d) Neutralise H^+ by adding OH^- on both sides of the equation:



(e) Combine H^+ and OH^- on the same side of the equation into H_2O :

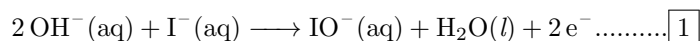


(f) Simplify the equation by removing common terms that appear on both sides of the equation:



- (g) Balance the charges by adding electrons to the more positive side:
 $2 \text{OH}^{-}(\text{aq}) + \text{I}^{-}(\text{aq}) \longrightarrow \text{IO}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^{-}$

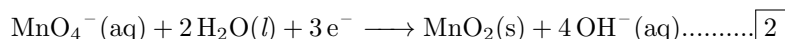
Half-equation for the oxidation reaction:



Next, we shall construct the half-equation for the reduction reaction.

- (a) Balance the number of moles of Mn atoms:
 $\text{MnO}_4^{-}(\text{aq}) \longrightarrow \text{MnO}_2(\text{s})$
- (b) Balance oxygen atoms by adding H_2O :
 $\text{MnO}_4^{-}(\text{aq}) \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$
- (c) Balance hydrogen atoms by adding H^{+} :
 $\text{MnO}_4^{-}(\text{aq}) + 4 \text{H}^{+}(\text{aq}) \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$
- (d) Neutralise H^{+} by adding OH^{-} on both sides of the equation:
 $4 \text{OH}^{-}(\text{aq}) + \text{MnO}_4^{-}(\text{aq}) + 4 \text{H}^{+}(\text{aq}) \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{OH}^{-}(\text{aq})$
- (e) Combine H^{+} and OH^{-} on the same side of the equation into H_2O :
 $\text{MnO}_4^{-}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{OH}^{-}(\text{aq})$
- (f) Simplify the equation by removing common terms that appear on both sides of the equation:
 $\text{MnO}_4^{-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^{-}(\text{aq})$
- (g) Balance the charges by adding electrons to the more positive side:
 $\text{MnO}_4^{-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^{-} \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^{-}(\text{aq})$

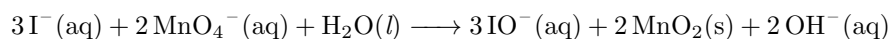
Half-equation for the reduction reaction:



The final step is to combine both half-equations to construct a complete redox reaction equation. To cancel out the electrons, we multiply equation $\boxed{1}$ by 3 and equation $\boxed{2}$ by 2.

$$\boxed{1} \times 3 + \boxed{2} \times 2:$$

The redox reaction equation:



Alternative method:

- (a) Determine oxidation states:
 I in I^{-} and IO^{-} is -1 and $+1$ respectively; Mn in MnO_4^{-} and MnO_2 is $+7$ and $+4$ respectively
- (b) Write the balanced half reactions:
 $\text{I}^{-}(\text{aq}) \longrightarrow \text{IO}^{-}(\text{aq}) + 2 \text{e}^{-}$; $\text{MnO}_4^{-}(\text{aq}) + 3 \text{e}^{-} \longrightarrow \text{MnO}_2(\text{s})$
- (c) Balance the electrons and combine:
 $3 \text{I}^{-}(\text{aq}) + 2 \text{MnO}_4^{-}(\text{aq}) \longrightarrow 3 \text{IO}^{-}(\text{aq}) + 2 \text{MnO}_2(\text{s})$
- (d) Balance charges with OH^{-} or H^{+} as necessary:
 $3 \text{I}^{-}(\text{aq}) + 2 \text{MnO}_4^{-}(\text{aq}) \longrightarrow 3 \text{IO}^{-}(\text{aq}) + 2 \text{MnO}_2(\text{s}) + 2 \text{OH}^{-}(\text{aq})$
- (e) Add H_2O to balance:
 $3 \text{I}^{-}(\text{aq}) + 2 \text{MnO}_4^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 3 \text{IO}^{-}(\text{aq}) + 2 \text{MnO}_2(\text{s}) + 2 \text{OH}^{-}(\text{aq})$

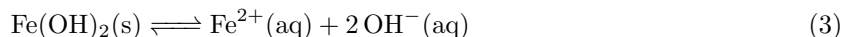
\therefore The ratio of hydroxide ions to iodide ions in the balanced equation is $\boxed{2 : 3}$ which is \boxed{D} .

38. Sodium ion has oxidation state of $+1$. Whilst, the charge of CO is zero because it is a neutral molecule. With the necessary information above, we can calculate the oxidation number of vanadium.

$$+1 + \text{V} + 6(0) = 0 \implies \text{V} = -1$$

So, the oxidation number of vanadium in the complex is $\boxed{-1}$ which is \boxed{A} .

39. $\text{Fe}(\text{OH})_2$ is sparingly soluble in water and will establish the following equilibrium in the solution (labelled as equation (3)):



The K_{sp} of the above equilibrium is unknown. However, we are given the half-reaction equations which we can use to compute K_{sp} .

We label both half-reactions:



Since $-(1)+(2)=(3)$, then

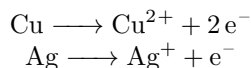
$$\begin{aligned} \Delta G_{(3)}^{\circ} &= -nFE_{\text{cell}}^{\circ} = -RT \ln K \\ \Delta G_{(3)}^{\circ} &= -2 \times 96500 \times [-(-0.44) + (-0.89)] = 8.69 \times 10^4 \\ -8.314 \times 298 \times \ln K_{\text{sp}} &= 8.69 \times 10^4 \\ K_{\text{sp}} &= 5.97 \times 10^{-16} \approx 6.0 \times 10^{-16} \end{aligned}$$

Therefore, the answer is \boxed{B} .

40. We first calculate the charge, Q using the equation $Q = It$, and then the total moles of electrons transferred during the electrolysis, using Faraday's constant, 96500 C/mol.

$$\begin{aligned} Q &= 0.150 \text{ A} \times 1429 \text{ sec} = 214.3 \text{ C} \\ \text{mol } e^{-} &= 214.3 \times \frac{1 \text{ mole } e^{-}}{96500 \text{ C}} \\ \text{mol } e^{-} &= 0.00222 \text{ mol } e^{-} \end{aligned}$$

The 0.00222 mole e^{-} is from the oxidation of 0.100 g alloy of copper and silver. The oxidation reactions for both metals is shown below:



Suppose that we have 'x' g of Cu. That is equivalent to $\frac{x}{63.5}$ moles Cu. From the oxidation reaction of Cu, the mole ratio between electrons and Cu is 2:1. Hence, we have $\frac{2x}{63.5}$ mole e^{-} . Since the total mass is 0.100 g, the mass of Ag is $(0.100 - x)$ g, which is equivalent to $\frac{0.100-x}{107.9}$ moles Ag. The mole ratio between electrons and silver is 1:1, which means that the moles of electrons from oxidation of silver is also $\frac{0.100-x}{107.9}$. Therefore, the total moles of electrons is

$$\frac{2x}{63.5} + \frac{0.100 - x}{107.9} = 0.00222 \text{ mol } e^{-}$$

Solving the equation for x , we get 0.0583 g of Cu. Now, the mass percentage of Cu in 0.100 g of alloy can be calculated.

$$\% \text{Cu} = \frac{0.0583}{0.100} \times 100\% = 58.3\%$$

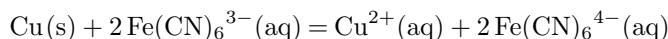
Hence, the answer is $\boxed{58.3\%}$ or \boxed{B} .

41. The cell potential (E_{cell}°) is defined as:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{right hand electrode}}^{\circ} - E_{\text{left hand electrode}}^{\circ}$$

This value is largest for option \boxed{D} .

42. The balanced redox reaction in the galvanic cell is



The discharging reaction is no longer spontaneous when the cell potential is zero. Therefore, we can have the following equation:

$$0 = (0.360 \text{ V} - 0.337 \text{ V}) - \frac{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}{2 \times 96500 \text{ C} \cdot \text{mol}^{-1}} \ln \left(\frac{[\text{Fe(CN)}_6^{4-}]^2 [\text{Cu}^{2+}]}{[\text{Fe(CN)}_6^{3-}]^2} \right)$$

Suppose the discharging reaction ceased after x mol/L of Cu^{2+} has produced:

$$0.023 = 1.28 \times 10^{-2} \ln \left(\frac{(0.200 + 2x)^2 (1.00 + x)}{(0.200 - 2x)^2} \right)$$

$$6.03 = \frac{(0.200 + 2x)^2 (1.00 + x)}{(0.200 - 2x)^2}$$

$$x = 0.0413 \text{ M}$$

You may ignore x compared to 1.00 to simplify the calculation.

$$[\text{Cu}^{2+}] = 1.00 \text{ M} + 0.0413 \text{ M} = \boxed{1.04 \text{ M}}$$

Therefore, the answer is \boxed{C} .

43. Because this question is asking for the "distance" between the nucleus and the 2s orbital of an atom, we want to pick the option that has the most protons, or the most attractive force (The 2s orbital is not changing, the valence orbital is). Therefore, the correct answer would be $\boxed{\text{Si}}$, or \boxed{D} .

- 44.
- Option **A** is **incorrect** because there is no 1p orbital.
 - Option **C** is **incorrect** because this is the electron configuration of nitrogen, and there is no way to excite the electrons in oxygen to this configuration.
 - Option **D** is **incorrect** because it's the electron configuration for a ground state oxygen, not an excited oxygen atom.
 - Option **B** is **correct** because electrons in oxygen's 2s orbital are excited to its 2p orbital. This satisfies the condition required by the question.

Hence, the answer is \boxed{B} .

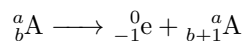
- 45.
- Option **A** is **correct** because alkali metals form 1+ ions and alkaline earth metals form 2+ ions. 2+ ions naturally have less repulsion between electrons and a smaller radius. Besides, alkaline earth metals have one more proton than alkali metals in the same period.
 - Option **B** is **incorrect** because alkaline earth metals have higher melting point due to more valence electrons (electron sea model) and smaller radius based on Coulomb's Law.
 - Option **C** is clearly **incorrect** because alkaline earth metals have greater first ionization energy since their effective nuclear charges are larger.
 - Option **D** is **incorrect** because alkaline earth metals have higher density due to higher molar mass and smaller ionic radius.

So, the correct answer is \boxed{A} .

46. We can first eliminate carbon and silicon since they are less electronegative than oxygen and sulfur. Usually electron affinity follows the trend of electronegativity, meaning that the more electronegative an atom is, the more negative its electron affinity is. But in this case, sulfur's larger atomic size greatly reduces the electron repulsion in oxygen, which ultimately results in a more negative electron affinity. Therefore, the answer is \boxed{D} .

47. When a d-block element gets ionized, electrons in the valence s orbital gets lost first. Thus, after counting we found that Cr^{2+} with an electron configuration of $3d^4$ has $\boxed{4}$ unpaired electrons according to Hund's rule. Therefore, the answer is \boxed{C} .

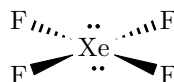
48. The general form of a beta decay is as follow since a neutron changes into a proton and an electron in beta decay:



So, we just need to find which option can get a stable nuclide after beta decay. The four nuclides that are produced after beta decay for all the options are ${}^{12}\text{N}$, ${}^{13}\text{O}$, ${}^{19}\text{F}$, and ${}^{22}\text{Mg}$, respectively. Obviously, ${}^{19}\text{F}$ is a stable isotope of F since it matches the relative atomic mass of F. Therefore, \boxed{C} is the correct answer.

49. After drawing the Lewis structure for all of these options, we find that BF_3 has a geometry of trigonal planar. CF_4 has a geometry of tetrahedral. NF_3 has a geometry of trigonal pyramidal. SF_6 has a geometry of octahedral. Due to symmetry, the dipole moments of each bond cancel nicely for trigonal planar, tetrahedral, and octahedral. Therefore, the only polar molecule in this question is $\boxed{\text{NF}_3}$, or \boxed{C} .

50. Let's draw the lewis structure of XeF_4 :



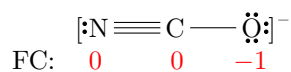
We can see conclude the geometry is $\boxed{\text{square planar}}$ according to the VSEPR model. The answer is therefore \boxed{A} .

51. The stability of the ions NCO^- and CNO^- is based on the formal charges (FC) of each atom in their Lewis dot structures. The formal charges help us decide the best possible Lewis dot structure among all possible resonance structures.

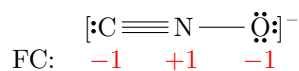
The formula of formal charge (FC) is shown below:

$$\text{FC} = \text{Number of valence } e^- \text{ in an atom} - \text{Number of lone } e^- - \text{Number of bonds}$$

The most stable or preferred structure for the cyanate ion, NCO^- is shown below:



Similarly, the preferred structure for the fulminate ion, CNO^- is also shown below:



Low formal charges mean that less electron transfer has occurred, and the structure represents the most stable form.

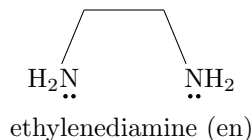
- Comparing the formal charges in both the ions, we see that the cyanate ion is more stable. Hence, **I** is **correct**.
- The cyanate ion, has a C–N triple bond and a C–O single bond. Triple bonds are stronger, and as a result shorter than single bonds, indicating that **II** is also **correct**.

Hence, the correct answer is \boxed{C} .

52. Isomer **1** and isomer **2** are the *cis*- and *trans*- isomer of 1,2-dichloroethane respectively. Isomer **1** has permanent dipole-permanent dipole forces and London Dispersion forces, while isomer **2** has only London Dispersion forces. Due to that, isomer **1** boils at higher temperature whereas isomer **2** boils at lower temperature. Hence, both isomers can be separated by fractional distillation.

Therefore, the answer is B.

53. • $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is known as ethylenediamine (en). It is a bidentate ligand and can form two dative covalent bonds with the central metal ion using the two lone pairs of electrons of the two N in the ligand. We present you the structure of en ligand.

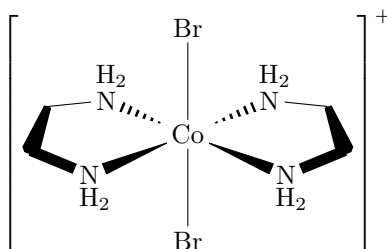


- Br^- is a monodentate ligand and can only form one dative covalent bond with the central metal ion.

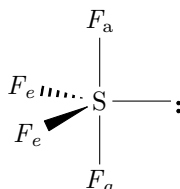
So, there are six electron pair donating atoms surrounding the central Co atom.

Therefore, the coordination geometry of $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Br}_2]^+$ is octahedral which is C.

One of the isomers of $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Br}_2]^+$ has the following geometry:



54. The see-saw geometry of SF_4 is shown below, with the axial F labeled F_a and the equatorial F as F_e .



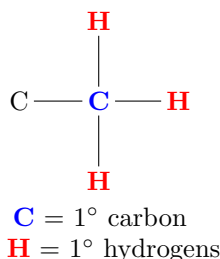
The lone electron pair (lp) is in the same plane as the equatorial F's. Based on the traditional valence bond theory, one would expect the central atom, S to be sp^3d hybridized, and the axial S–F bonds are slightly longer than those in the equatorial positions since the axial bonds experience greater repulsion. But actually the molecular orbital theory is applied to explain the bond length as follows: The central S take a sp^2 hybridization, forming two S–F bonds and a lone pair at the equatorial positions, as well as a unhybridized p orbital with two electrons. The unhybridized p orbital overlap with the 2p orbitals of two F atoms to form a "3-center 4-electrons" bond, so the axial S–F bonds are weaker because these two fluorines share bonding to the same p orbital on sulfur. Hence, the answer is A.

You may further read the "three-center four-electron bond" item in Wikipedia, here quotes part of its introduction as following:

"The 3-center 4-electron (3c-4e) bond is a model used to explain bonding in certain hypervalent molecules such as tetratomic and hexatomic interhalogen compounds, sulfur tetrafluoride, the xenon fluorides, and the bifluoride ion. It is also known as the Pimentel-Rundle three-center model after the work published by George C. Pimentel in 1951, which built on concepts developed earlier by Robert E. Rundle for electron-deficient bonding."

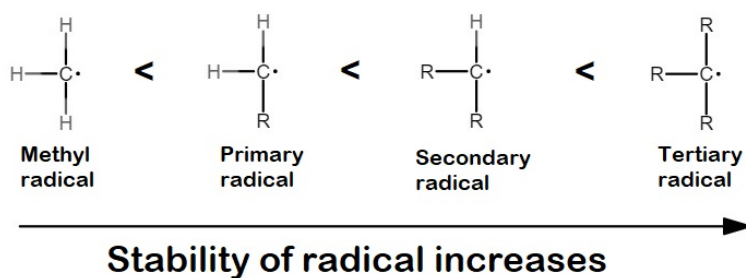
55. • According to the IUPAC rules, when assigning numbers for substituents in a compound, smaller numbers are preferred. With that, we can eliminate choice **A**. The methyl group should be assigned with number 3 as it is positioned on the third carbon.

- The branched hydrocarbon shown in the question is chiral. This is because the third carbon, starting from the right carbon atom, is bonded to four different substituents, hence it has no mirror plane. So, the statement in choice **B** is **correct**.
- The primary hydrogen is the hydrogen that is bonded to primary carbon. And a primary carbon is the one with only ONE carbon connected, as shown below:



We are able to count 9 primary hydrogens instead of 6 in the branched hydrocarbon, therefore choice **C** is omitted.

- Radical chlorination first involves formation of radicals. As shown below, the stability of radical increases when it is more and more substituted:



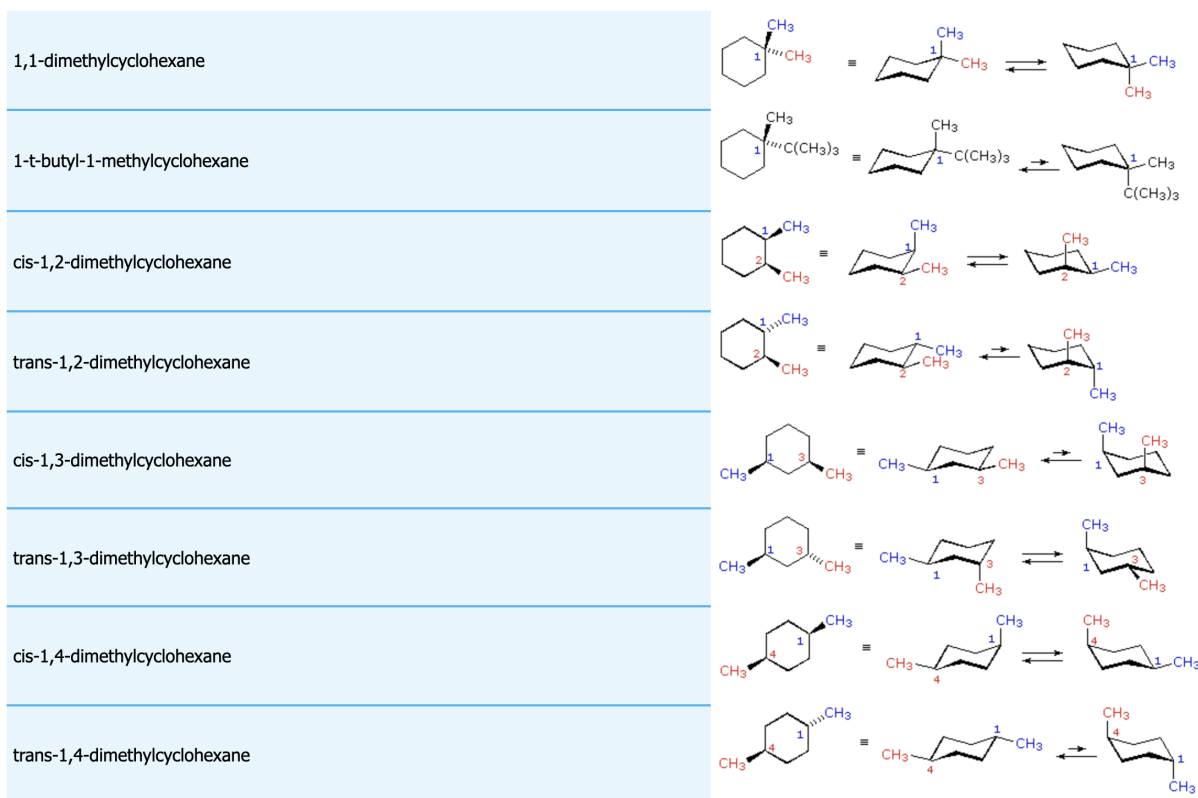
As such, the more stable radical will form the major product, while the less stable radical will form the minor product.

1-chloro-4-methylhexane is formed from primary radical (a less stable radical), hence it should be a minor product, NOT major product. So, choice **D** is **incorrect**.

Thus, the answer is **B**.

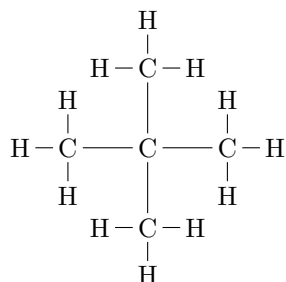
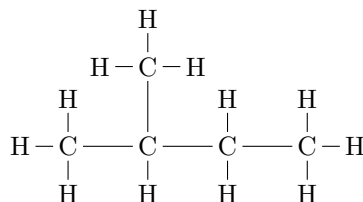
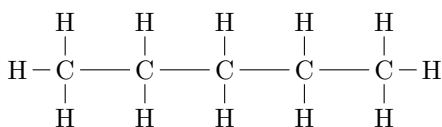
You may further read "hyperconjugation" for a detailed explanation of the stability of different radicals and carbocations.

56. The answer is **C**. As shown in the figure below, only the *trans*-1,2-dimethylcyclohexane has a chair conformation with both equatorial methyl groups. All other options have at least one axial methyl group. I recommend reading about the conformation of cyclohexane in an introductory organic textbook, such as Klein, or an online text, because this question does not really test on your problem solving skill, but rather, the basic definition of axial and equatorial bonds. Definitions like these are certainly better explained in a textbook.



source: LibreText

57. Let's first find the number of possible carbon skeletons for a hydrocarbon with five carbons:



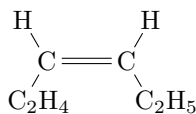
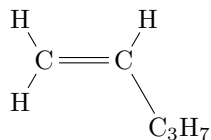
Now let's identify the functional groups presented in the compound by calculating its degree of unsaturation:

$$\text{DBE} = \frac{\text{C} \times 2 + 2 - \text{H} - \text{X} + \text{N}}{2} = 1$$

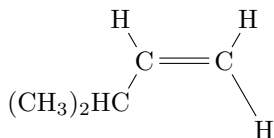
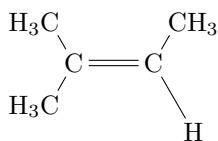
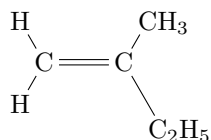
Where n is the degree of unsaturation, C is the number of carbons, X is the number of halogens, H is the number of hydrogen, and N is the number of nitrogen.

Because the compound is composed of only carbon and hydrogen and does not contain a ring (acyclic), there has to be 1 double bond to account for the DBE. Therefore, let's now investigate where the double bond can be placed:

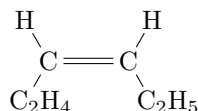
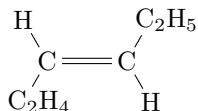
For the first carbon skeleton, we have:



For the second carbon skeleton, we have:



The last thing we need to do is to check for stereoisomers. For this question, none of the above molecules is chiral, but we need to check for *cis/trans* isomers due to the presence of a double bond. We found that there is one *cis/trans* isomer:



Therefore, there are in total $\boxed{6}$ isomers, and the answer should be \boxed{D} .

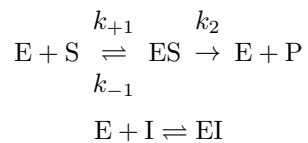
58. The answer is \boxed{B} . Acetal ($\text{RCH(R')}(OR'')_2$) can not be formed in basic condition from ketone or aldehyde because the leaving group " HO^- " is too bad. So acetals can only be formed under acidic condition, which is also commonly used for the protection of carbonyl group in organic synthesis. The other three products are all possible. A is a hemiacetal ($\text{RCH(R')}(OH)(OR'')$) formed by CH_3CHO reacting with 1 molecule of CH_3OH catalyzed either by acid or base. C is the aldol condensation product of two molecules of CH_3CHO , typically catalyzed by a base. D the further dehydration product of C, which is also commonly obtained as a final stable product of the aldol condensation as the $\text{C}=\text{C}$ is conjugated with the carbonyl group.

You may need to learn the chemistry of carbonyl in a systematic way to fully understand those advanced reactions above.

59. The correct answer is \boxed{A} . The hydrogen atom on the sp hybridized carbon in the propyne molecule is more acidic than the hydrogens on the sp^2 carbon atom in propene. In general, the more *s character* (i.e. the more dominant the orbital *s* is in the hybridization), the more electronegative the atom is ($\text{sp} > \text{sp}^2 > \text{sp}^3$). This is because the *s* orbital is lower in energy than the *p* orbitals. So the sp hybridized carbon best stabilizes the negative charge of the conjugate base, which explains why propynes are more acidic than propenes.

Regarding option A, the $\text{p}K_{\text{a}}$ s of propyne, ammonia, propene are: propene $>$ ammonia $>$ propyne, which explains why propyne can be deprotonated by NaNH_2 , while propene can't. Option B is incorrect since both propyne and propene can react with bromine readily through the addition of unsaturated carbon-carbon bond. The similar idea can be used to disapprove C. Propyne can propene can both undergo the acid-catalyzed hydration at $\text{pH} = 0$, though their products are different.

60. This problem tests your knowledge on the *Michaelis-Menten* kinetics. A **competitive inhibitor** competes with substrate for the same active site on the enzyme, forming some complex, EI, which doesn't continue to produce the product P . We can write the following reaction-scheme:



From the first graph, the dependence of $[P]$ over time is linear. However, The enzyme that is bound in a complex with the inhibitor, EI, is not available for binding with the substrate, so the effectiveness of the enzyme will be diminished. This will lead to a lower amount of $[P]$ formed per unit time. Furthermore, the presence of the inhibitor doesn't change the linear dependence of $[P]$ over time since the mechanism of the first sequence isn't altered. The correct answer is \boxed{B} .