Annotated Solution for USNCO Local Exam 2022

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Q1.

Difficulty: Easy

Learning Objectives: mass percent; stoichiometry

In order to calculate the percent mass of chlorine, we have to use the mass of chlorine to divide the compound mass of the compound.

For $\mathrm{KCl, Cl\%} = \frac{35.5}{39.0+35.5} = 47.7\%$

For $\mathrm{KClO, Cl\%} = \frac{35.5}{39.0+35.5+16.0} = 39.2\%$

For $\mathrm{KClO_2, Cl\%} = \frac{35.5}{39.0+35.5+16.0\times2} = 33.3\%$

For $\mathrm{KClO_3, Cl\%} = \frac{35.5}{39+35.5+16.0\times3} = 29.0\%$

Moreover, we can also approximate the result without the need of calculations. Since $M(\mathrm{Cl}) = 35.5\ \mathrm{g/mol}, M(\mathrm{K}) = 39.0\ \mathrm{g/mol}$ and $M(\mathrm{O}) = 16.0\ \mathrm{g/mol}$, we can conclude that $M(\mathrm{K}) \approx M(\mathrm{Cl}) \approx 2M(\mathrm{O})$. Thus, for Cl% to be smaller than 1/3, we can directly eliminate A, B and C with a simple approximation.

Thus, the answer is **$\mathrm{KClO_3}$ or D**.

Q2.

Difficulty: Easy

Learning Objectives: concept of mole; Avogadro's number

$n(\mathrm{FeS_2}) = \frac{m}{M} = \frac{3.00}{120.0} = 0.0250\ \mathrm{mol}$

$n(\mathrm{S}) = 2 \times n(\mathrm{FeS_2}) = 0.0250 \times 2 = 0.0500\ \mathrm{mol}$

$N(\mathrm{S}) = n(\mathrm{S}) \times N_\mathrm{A} = 0.0500 \times 6.02 \times 10^{23} = 3.01 \times 10^{22}$

Thus, the answer is **$\mathbf{3.01 \times 10^{22}}$ or C**.

Q3.

Difficulty: Medium

Learning Objectives: stoichiometry; limiting reactant

The reaction between H_2 and O_2:

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{H_2O(l)}$$

In the beginning, we have 0.50 L of H_2 and 0.50 L of He. When 1.00 L of oxygen is added, 0.50 L of hydrogen will react with 0.25 L of oxygen to form liquid water, leaving 0.75 L of oxygen unreacted. The mixture would contain 0.75 L of O_2 and 0.50 L of He, and the total volume is 1.25 L. From this, we can eliminate A, B and C, choosing **D** as the final answer.

Another approach to determining the answer is to consider the lowest volume it can reach. As there are 0.50 L of hydrogen initially present. The max amount of oxygen that can react is 0.25 L. Therefore, when 0.25 L of O_2 is added, all the hydrogen would be consumed, leaving only 0.50 L of He left, which would also give us **D** as the answer.

Difficulty: Easy

Learning Objectives: molarity; dissociation of electrolytes

Q4.

$[NO_3^-] = 2[Cu(NO_3)_2]$

$\therefore [NO_3^-] = 2 \times 0.25 = 0.50\ \text{M}$

The answer is **0.50 M or D**.

Difficulty: Easy

Learning Objectives: stoichiometry; molar mass

Q5.

$$n(\text{C}) = n(CO_2) = \frac{m}{M} = \frac{0.383}{12.0 + 16.0 \times 2} = 0.00870\ \text{mol}$$

Since we now know the amount of substance of carbon, we will know the molar mass of the transition metal carbonate compound.

$$\therefore M(MCO_3) = \frac{m}{n} = \frac{1.000}{0.00870} = 115\ \text{g/mol}$$

$$\therefore M(\text{M}) = 115 - (12 + 16 \times 3) = 55\ \text{g/mol}$$

In all the four choices, **Mn or A** is the metal with a molar mass of 55 g/mol.

Difficulty: Easy

Learning Objectives: stoichiometry of precipitation reactions; limiting reactants

Q6.

When the two solutions are mixed, Na^+ and NO_3^- does not form a precipitate. But Ba^{2+} and SO_4^{2-} forms a precipitate $BaSO_4$.

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$$

$n(Ba^{2+}) = 14.0 \times 10^{-3} \times 0.53 = 0.0074\ \text{mol}$

$n(SO_4^{2-}) = 16.0 \times 10^{-3} \times 0.44 = 0.00704\ \text{mol}$

Since the stoichiometric ratio of Ba^{2+} and SO_4^{2-} in $BaSO_4$ is 1:1 and more Ba^{2+} is initially present, there will be more Ba^{2+} when the solution becomes saturated.

Thus, the amount of $\mathbf{SO_4^{2-}}$ **or D** will be the least in the final solution.

Difficulty: Easy

Learning Objectives: color of common ions

Q7.

A. $\mathbf{NaClO_4}(aq)$ is colorless.

B. $K_2CrO_4(aq)$ is yellow.

C. $Ni(NO_3)_2(aq)$ is green.

D. $CuSO_4(aq)$ is blue.

Difficulty: Medium

Learning Objectives: low solubility of $Ca(OH)_2$; acid-base neutralization; color change of indicator (phenolphthalein)

Q8.

As HCl is added to the solution, it will react with the precipitate $Ca(OH)_2$ forming H_2O and Ca^{2+} and Cl^-. Allowing the solution to turn from cloudy to clear. With 0.1 mol of HCl added and 0.01 mol $Ca(OH)_2$ initially present, the solution will turn acidic. Phenolphthalein is pink under basic but colorless under neutral or acidic conditions. Therefore, the solution will also become colorless. Thus, **only II or B** is correct.

Q9.

Difficulty: Easy

Learning Objectives: reading of buret; volumetric glassware

The reading of the burette increases from top to bottom. Thus, the best estimated measurement of the volume is **1.26 mL or B**. Please be aware to include two decimal places including the last digit estimated when recording the readings for burettes.

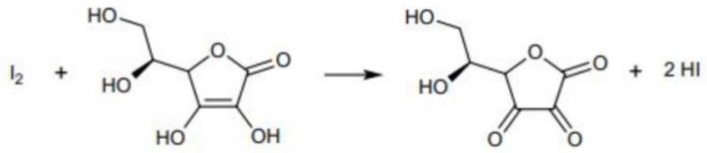
Q10.

Difficulty: Hard

Learning Objectives: iodometry; starch as indicator

There are two different methods regarding the titration with iodine, direct iodometry (iodimetry) and indirect iodometry. Direct iodometry contains a single step, which is the reduction of I_2/I_3^- to I^-, with a starch endpoint. While indirect iodometry require two steps, the first is the oxidation of I^- to I_2/I_3^-, then the titration of thiosulfate with I_2/I_3^-, with a starch endpoint. The question is asking for direct iodometry, a single step titration with I_3^-. Which requires the analyte to be a stronger reducing agent than I_3^-.

B, C and D are commonly used examples for direct iodometry. For B, ascorbic acid reacts with I_2/I_3^- to form dehydroascorbic acid and I^-.



For C, sulfite reacts with I_2/I_3^-, while sulfate don't.

$$SO_3^{2-} + I_2 + H_2O \rightarrow HSO_4^- + 2I^- + H^+$$

For D, thiosulfate reacts with I_2/I_3^-, which is also the common secondary step for indirect iodometry.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

There are two reasons why A cannot be used for iodometry. The first reason is that it can't be done with direct iodometry. No matter the composition of the alloy is, it would always require indirect iodometry. Since metal ions can't be reduced by I_3^-. The second reason is due to the composition of the alloy, which is Ni/Co. The reduction potential of Ni^{2+}/Co^{2+} are –0.25 V and –0.28 V respectively, However, the reduction potential of I_3^- is 0.535 V. Thus, neither Ni^{2+}/Co^{2+} can be reduced by I_3^-. And the answer is **Analysis of nickel content in a Ni/Co alloy or A**.

Extension:

If we are going to analyze the copper content in a copper-containing alloy. Indirect iodometry will work. We need to first dissolve the alloy in concentrated nitric acid, which converts all metals into ions including Cu. Then we can add excess amount of KI to the mixture. This is because Cu^{2+} reacts with I^- to form I_2 or I_3^- and CuI(s) with a $K_{sp} = 1.3 \times 10^{-12}$. Then standard thiosulfate solution is added to titrate the produced I_2 or I_3^- to the starch endpoint. The amount of thiosulfate needed reflects the amount of I_2, which further gives the amount of the copper ions and thus the copper content in the alloy. This is one of the most quintessential examples for indirect iodometry.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + 2I_2$$

Difficulty: Medium

Learning Objectives: reactivity of alkali metals

Q11.

Sodium is usually stored in kerosene or mineral oil, it is very reactive and reacts with O_2 and moisture in the air but does not react with kerosene. The answer is **Mineral oil or B**.

Sodium will react with vigorously with water, forming H_2 gas and NaOH. It will also react with ethanol to produce H_2 and sodium ethoxide CH_3CH_2ONa. Sodium reacts with CCl_4 to produce NaCl and C.

Difficulty: Medium

Learning Objectives: calorimetry; error analysis

Q12.

This is a coffee-cup calorimeter, in which $\Delta H = -q$. Since the actual mass is larger than the weighed mass, according to $q = c \times m \times \Delta T$, $|\Delta T|$ is smaller than the value without water. Therefore, the measured $\Delta H^\circ_{\text{soln}}$ is smaller than the actual $\Delta H^\circ_{\text{soln}}$. The answer is **Calculated $\Delta H^\circ_{\text{soln}}$< True $\Delta H^\circ_{\text{soln}}$ or C.**

Difficulty: Medium

Learning Objectives: phase change; ice vs liquid water; thermal contraction of water

Q13.

Solidification of water is an exothermic process, so **Heat flows out of the system or A** is the answer. As water solidifies, its vapor pressure decreases, and its hydrogen bonds become stronger. The volume of the system also increases since $\rho_{\text{ice}} < \rho_{\text{water}}$. So, choices B, C, and D are all incorrect.

Difficulty: Medium

Learning Objectives: solubility and intermolecular forces; hydrogen bonds

Q14.

Both A, B, C, D have the same molar mass, so the London dispersion forces between the four should be the same. However, only **A** can form two hydrogen bonds per molecule with water, which will make it more soluble in water. Thus, the correct answer is **A**.

Difficulty: Medium

Learning Objectives: intermolecular forces; hydrogen bonds

Q15.

HF can make hydrogen bonds with each other, overweighing the fact that it has the smallest molar mass and allowing it to have the highest boiling point. From HCl to HI, none of compounds experience hydrogen bonding and their molecular mass increases. Allowing the London dispersion forces to get stronger, overcoming the fact that the dipole-dipole interaction becomes weaker. Thus, the boiling point of $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$. The answer is therefore **HCl or B**.

Difficulty: Hard

Learning Objectives: phase diagram and critical point; ideal gas law; vapor pressure and its dynamic equilibrium

Q16.

As this is a sealed container, the volume will remain constant throughout the process. If only C_2H_6 was present, then the pressure inside the container at 150 K will equal to the vapor pressure of C_2H_6, which is 0.10 atm. However, the pressure at 150 K is in fact 0.37 atm, so it can't be A.

Moreover, since the critical point of Ne is 44 K, at temperatures higher than 44 K, the pressure of Ne should remain constant. Therefore, if only Ne was present in the container, as the temperature halved, the pressure should also be halved according to $pV = nRT$. However, the pressure decreased more than half, showing that Ne was not the sole sample. Thus, combining the two analyses, we can conclude that the sample is **A mixture of ethane and neon or C.**

Q17.

Difficulty: Medium

Learning Objectives: phase diagram and triple point; density comparison based on phase diagram

According to the phase diagram, under 1 atm, monoclinic sulfur turns into liquid, but not solid, so A is incorrect. The boundary line between monoclinic sulfur and rhombic sulfur has a positive slope, so under the same temperature, when pressure increases, the volume will be compressed and rhombic sulfur will have a smaller volume than monoclinic sulfur, which means that rhombic sulfur is more dense than monoclinic sulfur, and B is incorrect. At temperatures above 119 ℃, monoclinic sulfur can still exist in equilibrium with liquid and rhombic sulfur at higher pressures, so C is incorrect. Under constant pressure, the temperature for monoclinic sulfur to exist is higher than the temperature for rhombic sulfur to exist, more heat is needed to convert rhombic sulfur to monoclinic sulfur, so **the conversion of rhombic sulfur to monoclinic sulfur is endothermic or D** is correct.

Q18.

Difficulty: Medium

Learning Objectives: solid models; density calculation of unit cells

Since aluminum crystallizes in a face-centered cubic unit cell, each unit cell will contain four aluminum atoms. For each unit cell:

$$V(\text{unit cell}) = a^3 = (405 \times 10^{-10})^3 = 6.64 \times 10^{-23}\ \text{cm}^3$$

$$m(\text{unit cell}) = \frac{M}{N_\text{A}} \times 4 = \frac{27.0}{6.02 \times 10^{23}} \times 4 = 1.79 \times 10^{-22}\ \text{g}$$

$$\rho(\text{unit cell}) = \frac{m}{V} = \frac{1.79 \times 10^{-22}}{6.64 \times 10^{-23}} = 2.70\ \text{g/cm}^3$$

Thus, the answer is $\mathbf{2.70\ g/cm^3}$ **or C**.

Q19.

Difficulty: Medium

Learning Objectives: calorimetry; heat of fusion and vaporization

For a closed system, $|q_\text{in}| = |q_\text{out}|$.

$$|q_\text{ice}| = |\Delta H_\text{fus} \times m + c \times m \times \Delta T| = 100.0 \times 334 + 4.184 \times 100.0 \times (40.0 - 0.00) = 50.1\ \text{kJ}$$

$$m(\text{water}) = \frac{|q_\text{ice}|}{\Delta H_\text{vap}} = \frac{50.1 \times 10^3}{2260} = 22.2\ \text{g}$$

Thus, the answer is **22.2 g or C**.

Q20.

Difficulty: Medium

Learning Objectives: Hess's law; enthalpy of formation; reaction enthalpy

$$2\text{Fe(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} \quad \Delta H_\text{f}^\circ(\text{Fe}_2\text{O}_3) = -825.5\ \text{kJ/mol}$$

$$\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta H_\text{rxn}^\circ(2) = -283.0\ \text{kJ/mol}$$

$$\text{Fe}_2\text{O}_3\text{(s)} + 3\,\text{CO(g)} \rightarrow 2\,\text{Fe(s)} + 3\,\text{CO}_2\text{(g)} \quad \Delta H_\text{rxn}^\circ(3) = ???$$

By taking a close look at the reactions we have and what we are looking for, it is not hard to discover that the third reaction is a certain combination of the first two. When three times of the second reaction subtracts the first reaction, we will get the reaction we are looking for.

$$3\text{CO(g)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow 3\text{CO}_2\text{(g)} \quad \Delta H_\text{rxn}^\circ(2)' = \Delta H_\text{rxn}^\circ(2) \times 3 = -283.0 \times 3 = -849\ \text{kJ/mol}$$

Therefore, according to Hess Law, we can conclude that $\Delta H^\circ_{\text{rxn}}(3) = 3\,\Delta H^\circ_{\text{rxn}}(2) - \Delta H^\circ_{\text{f}}(\text{Fe}_2\text{O}_3) = 3 \times -283.0 - (-825.5) = -23.5$ kJ/mol. The answer is $\mathbf{-23.5\ kJ/mol}$ **or A**.

Difficulty: Hard

Learning Objectives: thermodynamics; internal energy vs enthalpy and heat

Q21.

According to the first law of thermodynamics, $\Delta E = q + w$. For a bomb calorimeter, the volume remains constant throughout the process, $\Delta V = 0$. $w = -p\Delta V = 0$, and $\Delta E = q$, so *I* is a correct statement. According to the definition of enthalpy $H = E + pV$, $\Delta H = \Delta E + \Delta(pV) = \Delta E + p\Delta V + V\Delta p$. As $\Delta V = 0$, we have $\Delta H = \Delta E + V\Delta p$, and $\Delta E = \Delta H - V\Delta p$. Thus, *II* is a correct statement. Therefore, the answer is **Both *I* and *II* or C**.

Difficulty: Easy

Learning Objectives: enthalpy change and bond energy

Q22.

$$\Delta H° = \Delta H^\circ_{\text{BDE}}(\text{cyclopropane})_{\text{tot}} - \Delta H^\circ_{\text{BDE}}(\text{propene})_{\text{tot}} = -32\ \text{kJ/mol}$$

$$\because \Delta H^\circ_{\text{BDE}}(\text{C–H}_{\text{propene}}) = \Delta H^\circ_{\text{BDE}}(\text{C–H}_{\text{cyclopropene}})$$

$$\therefore \Delta H^\circ_{\text{BDE}}(\text{cyclopropane}) - \Delta H^\circ_{\text{BDE}}(\text{propene})$$

$$= 3 \times \Delta H^\circ_{\text{BDE}}(\text{C–C}_{\text{cyclopropane}}) - \Delta H^\circ_{\text{BDE}}(\text{C–C}_{\text{propene}}) - \Delta H^\circ_{\text{BDE}}(\text{C=C}_{\text{propene}})$$

$$= 3 \times \Delta H^\circ_{\text{BDE}}(\text{C–C}_{\text{cyclopropane}}) - 345 - 611 = -32\ \text{kJ/mol}$$

$$\Delta H^\circ_{\text{BDE}}(\text{C–C}_{\text{cyclopropane}}) = \frac{-32 + 611 + 345}{3} = 308\ \text{kJ/mol}$$

The answer is $\mathbf{308\ kJ/mol}$ **or A**.

Difficulty: Hard

Learning Objectives: $\Delta G°=\Delta H°–T\Delta S°= –RT\ln K$; spontaneity; kinetics and Arrhenius factor

Q23.

According to the equation below, since the two reactions have a similar change in enthalpy, the one with the larger entropy change will have a more negative free energy value and therefore will be more spontaneous under the same temperature conditions.

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K_{\text{eq}}$$

Thus, $K_{\text{eq}(2)}$ should be larger than $K_{\text{eq}(1)}$ and *I* is incorrect.

Both enthalpy and entropy are thermodynamic properties, which does not relate to kinetic properties. We cannot conclude about the Arrhenius pre-factor based on the information provided, so *II* is incorrect. The answer is **Neither *I* nor *II* or D**.

Difficulty: Medium

Learning Objectives: sign of entropy change; entropy comparison of isomers (cycloalkanes vs alkenes)

Q24.

As all reactants and products are liquid, both A and D has a net decrease in moles from reactants to products, which means that the entropy decreases in the two cases. Cyclic compounds have less disorder compared to acyclic compounds, since acyclic compounds have more conformations compared to cyclic compounds. Thus, **B** is the answer with an increase in entropy.

Q25.

Difficulty: Easy

Learning Objectives: relative reaction rate

$$14H^+(aq) + Cr_2O_7^{2-}(aq) + 6Cl^-(aq) \rightarrow 2Cr^{3+}(aq) + 3Cl_2(aq) + 7H_2O(l)$$

In the chemical equation above, the stoichiometric ratio between $Cl^-(aq)$ and $Cr^{3+}(aq)$ is 3:1. Therefore, the rate of consumption of $Cl^-(aq)$ is three times the rate of formation of $Cr^{3+}(aq)$.

$$\frac{d[Cr^{3+}(aq)]}{dt} = -\frac{1}{3} \times \frac{d[Cl^-(aq)]}{dt} = -\frac{1}{3} \times (-0.37) = 0.12 \text{ mol/(L min)}$$

The correct answer is **Increasing by $\mathbf{0.12\ mol\ L^{-1}\ min^{-1}}$ or A**.

Q26.

Difficulty: Medium

Learning Objectives: integrated rate law and half-life of first-order reactions

All radioactive decay reactions are first order. Therefore,

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{272 \text{ d}} = 0.00255 \text{ d}^{-1}$$

Based on the integrated rate law for first-order reactions

$$\ln[Co]_t = -kt + \ln[Co]_0$$

$$t = \frac{1}{k} \times \ln\frac{[Co]_0}{[Co]_t}$$

Since $[Co]_t$ is 38% of $[Co]_0$,

$$t = \frac{1}{0.00255} \times \ln\frac{100\%}{38\%} = 380 \text{ d}$$

Thus, the answer is **380 d or D**.

Q27.

Difficulty: Easy

Learning Objectives: Arrhenius equation (rate vs temperature); collision model

Based on the Arrhenius equation,

$$k = Ae^{\frac{-E_a}{RT}}$$

As temperature increases, $\frac{-E_a}{RT}$ becomes larger and less negative, increasing the value of the rate constant. Moreover, as temperature increases, the average kinetic energy among the particles increase, allowing for a higher portion of particles that have the sufficient activation energy for a reaction to occur upon collision. Thus, the answer is **C**.

Q28.

Difficulty: Medium

Learning Objectives: rate law derivation; pre-equilibrium approximation; rate-determining step

By looking at the proposed mechanism, we can conclude that the second step is the slowest of all the three elementary reactions and is the rate-determining step. Thus, the rate law will have to be first order regarding $[N_2O_2]$ and $[H_2]$, which can lead us to the answer **B**, the only option with a first order $[H_2]$. Furthermore, since $[N_2O_2]$ is an intermediate, we will have to replace it with reactants. Based on the fast and reversible first elementary reaction in the mechanism, pre-equilibrium can be established, where we can conclude that $k_f[NO]^2 = k_r[N_2O_2]$. Thus, we can replace $[N_2O_2]$ with $[NO]^2$, which would lead us to the final rate law:

Rate $= k[NO]^2[H_2]$, the answer is therefore **B**.

Difficulty: Medium

Learning Objectives: pseudo kinetic analysis; linear relationship of reactions with different orders

Q29.

Since $[B]_0 \gg [A]_0$, a pseudo rate law may be established.

$$\text{Rate} = k_{\text{obs}}[A]^{\alpha}$$

$$k_{\text{obs}} = k[B]^{\beta}$$

As $\frac{1}{[A]}$ is linear with time, the order with respect to A is second and $\alpha = 2$. Moreover, since the slope (k_{obs}) is independent with [B], then B is zeroth order and $\beta = 0$. Therefore, the rate law is $\mathbf{Rate = k[A]^2}$ **and C** is the answer.

Difficulty: Medium

Learning Objectives: mechanism of catalysts; rate vs surface area

Q30.

Catalysts does not affect the thermodynamic properties of a reaction, so we can eliminate C and D. Catalysts are part of the reaction's mechanism, where it is initially consumed and later produced, having no net changes in mass throughout the reaction. Thus, when using a catalyst with a larger mass or surface area, the reaction will proceed easier, having a lower activation energy and a faster rate. Thus, **the rate of the reaction would increase if more finely divided platinum were used because the reaction depends on the surface area of the catalyst or B** is correct.

Difficulty: Easy

Learning Objectives: K_{sp} and solubility

Q31.

We can express the solubility product as follows.

$$K_{\text{sp}} = [Pb^{2+}][I^-]^2$$

Since PbI_2 solution is saturated, the concentration of I^- is twice as large as the concentration of Pb^{2+}. Thus, $[I^-]$ can be solved using the following equations.

$$[I^-] = 2[Pb^{2+}]$$

$$K_{\text{sp}} = [Pb^{2+}](2[Pb^{2+}])^2 = 4[Pb^{2+}]^3$$

$$[Pb^{2+}] = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = \sqrt[3]{\frac{1.4 \times 10^{-8}}{4}} = 1.5 \times 10^{-3}\ \text{M}$$

$$[I^-] = 2 \times (1.5 \times 10^{-3}) = 3.0 \times 10^{-3}\ \text{M}$$

The correct answer is **D**.

Difficulty: Medium

Learning Objectives: dynamic equilibrium and K_P

Q32.

The expression of the equilibrium constant of the equation is shown below, which is only dependent on the temperature:

$$K_{\text{p}} = P_{CO_2} P_{H_2O}$$

According to the expression, the amount of $NaHCO_3$(s) does not affect the pressure of CO_2 and H_2O in the vessel unless it is fully decomposed. Since the decomposition of 50.0 g sodium bicarbonate reaches to the equilibrium, remnants must exist. Thus, the decomposition of 100.0 g sodium bicarbonate is not fully decomposed so the total pressure keeps the same. The correct answer is **6.25 atm**, which is **A**.

Q33.

Difficulty: Medium

Learning Objectives: acidity of salt solutions

$NaNO_2$ is a strong electrolyte, so it dissolves completely in water. Na^+ is a spectator in the solution, which has a relatively high concentration. NO_2^- is the conjugated base of a weak acid, which hydrolyzed with water. The reaction is shown below.

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$$

HNO_2 concentration is approximately the same as OH^- concentration, which are both higher the concentration of H_3O^+ because the solution is basic. Thus, the correct answer is $\mathbf{H_3O^+}$, which is **D**.

Q34.

Difficulty: Medium

Learning Objectives: K_{sp} and molar solubility

We can solve $[Ag^+]$ for each choice as follows.

$[Ag^+]$ in AgCl solution:

$$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2$$

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\ \text{M}$$

$[Ag^+]$ in Ag_2CrO_4 solution:

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = \frac{1}{2}[Ag^+]^3$$

$$[Ag^+] = \sqrt[3]{2 \times K_{sp}} = \sqrt[3]{2 \times (1.1 \times 10^{-12})} = 1.3 \times 10^{-4}\ \text{M}$$

$[Ag^+]$ in AgBr solution:

$$K_{sp} = [Ag^+][Br^-] = [Ag^+]^2$$

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{5.0 \times 10^{-13}} = 7.1 \times 10^{-7}\ \text{M}$$

$[Ag^+]$ in Ag_2SO_3 solution:

$$K_{sp} = [Ag^+]^2[SO_3^{2-}] = \frac{1}{2}[Ag^+]^3$$

$$[Ag^+] = \sqrt[3]{2 \times K_{sp}} = \sqrt[3]{2 \times (1.5 \times 10^{-14})} = 3.1 \times 10^{-5}\ \text{M}$$

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

Q35.

Difficulty: Hard

Learning Objectives: pH calculation of amphoteric solutions

The expression of two equilibrium constant is shown below, respectively.

$$K_{a,NH_4^+} = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$K_{a,HF} = \frac{[F^-][H^+]}{[HF]}$$

$$K_{a,NH_4^+} \times K_{a,HF} = \frac{[NH_3][F^-][H^+]^2}{[NH_4^+][HF]}$$

Now if we consider the following equilibrium.

$$NH_4^+ + F^- \rightleftharpoons NH_3 + HF$$

Then we can say that

$$[\mathrm{NH_4^+}] \approx [\mathrm{F^-}]$$
$$[\mathrm{NH_3}] \approx [\mathrm{HF}]$$

Thus, pH can be solved as follows.

$$K_{\mathrm{a,NH_4^+}} \times K_{\mathrm{a,HF}} = \frac{[\mathrm{NH_3}][\mathrm{F^-}][\mathrm{H^+}]^2}{[\mathrm{NH_4^+}][\mathrm{HF}]} = [\mathrm{H^+}]^2$$

$$[\mathrm{H^+}] = \sqrt{K_{\mathrm{a,NH_4^+}} \times K_{\mathrm{a,HF}}} = \sqrt{(5.6 \times 10^{-10}) \times (6.8 \times 10^{-4})} = 6.2 \times 10^{-7}$$

$$\mathrm{pH} = 6.21$$

The correct answer is **C**.

We may further extend to get an important conclusion that the pH of an amphoteric solution is the average of the two pK_as of the acidic dissociation and its conjugate acid, regardless of its concentration. Taking $NaHCO_3$(aq) as an example, the acidic dissociation of HCO_3^-(aq) is $\mathrm{HCO_3^-} \rightleftharpoons \mathrm{CO_3^{2-}} + \mathrm{H^+}$, which has a p$K_a$ = pK_{a2} of H_2CO_3, the conjugate acid of HCO_3^- is H_2CO_3, which has a pK_a = pK_{a1} of H_2CO_3. So, the pH = ½ (pK_{a1} + pK_{a2}) = ½ (6.37+10.33) = 8.35, which is consistent with the basic properties of $NaHCO_3$.

Difficulty: Medium
Learning Objectives: titration and titration curve; half-equivalence point

Q36.

According to the titration curve, the titration reaches to its equivalence point when around 17.3 mL HCl is added. Since all four anions are conjugate base of a monoprotic acid, we can find out the molar mass of the salt using following equations.

$$n(\mathrm{Salt}) = n(\mathrm{HCl})$$

$$n(\mathrm{Salt}) = 17.3\ \mathrm{mL} \times 0.500\ \mathrm{M} \times \frac{1.000\ \mathrm{L}}{1000\ \mathrm{mL}} = 8.65 \times 10^{-3}\ \mathrm{mol}$$

$$\text{Molar mass} = \frac{m(\mathrm{Salt})}{n(\mathrm{Salt})} = \frac{1.000\ \mathrm{g}}{8.65 \times 10^{-3}\ \mathrm{mol}} = 116\ \mathrm{g/mol}$$

There is an alternative solution. The titration reaches to its half equivalence point when around 8.5 mL HCl is added. At this point, $\mathrm{pH} = \mathrm{p}K_\mathrm{a} = 9.9$. Thus, the correct answer is **C**.

Difficulty: Easy
Learning Objectives: concept of oxidation state

Q37.

The sum of all oxidation states of each element in a compound must be 0. We can easily assign oxidation states for every element except for manganese. The oxidation state for each Ba is +2, -2 for each O, and x for each Mn.

$$2 \times (+2) + x \times 5 + 10 \times (-2) = 0$$
$$x = 3.2$$

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

Difficulty: Easy
Learning Objectives: oxidation states and concept of redox

Q38.

The oxidation state of nitrogen in HNO_3 is +5 and that in NO is +2. The oxidation state of nitrogen changes from +5 to +2. Thus, **nitrogen** is reduced. The correct answer is **C**.

Q39.

Difficulty: Easy
Learning Objectives: standard cell potential and reduction potentials

Since a spontaneous galvanic cell must have a positive cell potential, the first half-equation is cathode, and the second half-equation is anode. Thus, *II* in correct. The standard cell potential can be calculated as follows.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{ano}} = -0.28 - (-0.34) = 0.06\ \text{V}$$

Thus, choice *I* is incorrect. The correct answer is **B**.

Q40.

Difficulty: Medium
Learning Objectives: electrolysis and Faraday's law

We can do dimensional analysis with m g of sodium. Note that the oxidation state of sodium in NaCl is +1, so each sodium ion gain $1\ e^-$.

$$m\ \text{g} \times \frac{1\ \text{mol Na}}{22.99\ \text{g}} \times \frac{1\ \text{mol e}^-}{\text{mol Na}} \times \frac{96500\ \text{C}}{\text{mol e}^-} \times \frac{1\ \text{s}}{10.0\ \text{C}} \times \frac{1\ \text{min}}{60\ \text{s}} = 10.0\ \text{min}$$

$$7.00\ m = 10.0$$

$$m = 1.43\ \text{g}$$

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

Q41.

Difficulty: Medium
Learning Objectives: qualitative analysis of Nernst equation

According to the Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ must be minimized to maximize E_{cell}. Thus, the answer is **B**.

Q42.

Difficulty: Hard
Learning Objectives: Nernst equation – calculation of nonstandard reduction potential; *E*-pH diagram

The half reaction of oxygen under acidic and basic conditions are shown as follows.

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O} \qquad E^\circ_{\text{acidic}} = +1.23\ \text{V}$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^- \qquad E^\circ_{\text{basic}} = \ ?\ \text{V}$$

We notice that if we add four times of the equation below to the half reaction of oxygen under acidic condition, we can get the half reaction of oxygen under basic condition.

$$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \qquad K_{\text{w}} = 1.0 \times 10^{-14}$$

By Hess's law, we can solve the standard reduction potential of the aimed equation as follows.

$$\Delta G^\circ_{\text{acidic}} = -nFE^\circ_{\text{acidic}} = -4\ \text{mol} \times 96500\frac{\text{C}}{\text{mol}} \times 1.23\ \text{V} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = -475\ \text{kJ/mol}$$

$$\Delta G^\circ_{\text{w}} = -RT\ln K_{\text{w}} = -8.314\frac{\text{J}}{\text{mol}\cdot\text{K}} \times 298\ \text{K} \times \ln(1.0 \times 10^{-14}) \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 79.9\ \text{kJ/mol}$$

$$\Delta G^\circ_{\text{basic}} = \Delta G^\circ_{\text{acidic}} + 4 \times \Delta G^\circ_{\text{w}} = -475\frac{\text{kJ}}{\text{mol}} + 4 \times 79.9\frac{\text{kJ}}{\text{mol}} = -155\ \text{kJ/mol}$$

$$E^\circ_{\text{basic}} = -\frac{\Delta G^\circ_{\text{basic}}}{nF} = -\frac{-155\frac{\text{kJ}}{\text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}}}{4\ \text{mol} \times 96500\frac{\text{C}}{\text{mol}}} = +0.40\ \text{V}$$

An alternate way to solve the problem is to interpret the basic half equation ($[H^+] \neq 1.0$ M) as the *nonstandard* state of the acidic one ($[H^+] = 1.0$ M) and then apply the Nernst equation to the half reaction.

$$E°_{\text{basic}} = E_{O_2/H_2O}\ ([H^+] \neq 1.0\ \text{M}) = E°_{\text{acidic}} - \frac{RT}{nF}\ln\frac{1}{p_{O_2}[H^+]^4}$$

$P_{O_2} = 1$ bar at standard state for both $[H^+] = 1.0$ M and $[OH^-] = 1.0$ M, the equation above can be simplified into:

$$E°_{\text{basic}} = E°_{\text{acidic}} - \frac{RT}{nF}\ln\frac{1}{[H^+]^4} = E°_{\text{acidic}} - \frac{2.303 \times RT}{nF}\log_{10}\frac{1}{[H^+]^4}$$

When the second half reaction is at its own standard state, $[OH^-] = 1.0$ M, and pH=14.0, substitute into the equation above, we can get the same answer.

$$E°_{\text{basic}} = 1.23 - \frac{2.303 \times 4 \times 8.314 \times 298}{4 \times 96500} \times 14.0 = 0.40\ \text{V}$$

Difficulty: Medium
Learning Objectives: energy and wavelength of photons

Q43.

To find out the wavelength of a single photon, we must solve for the energy carried by each photon using following equation.

$$E_{\text{photon}} = \frac{E}{N_A} = \frac{1.00 \times 10^3\ \frac{\text{kJ}}{\text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}}}{6.02 \times 10^{23}\ \text{mol}^{-1}} = 1.66 \times 10^{-18}\ \text{J}$$

Then, wavelength of a photon can be solved as follows.

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

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\ \text{J} \cdot \text{s} \times \left(3.00 \times 10^8\ \frac{\text{m}}{\text{s}}\right)}{1.66 \times 10^{-18}\ \text{J}} = 1.20 \times 10^{-7}\ \text{m}$$

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

Difficulty: Easy
Learning Objectives: electron configuration of ions; isoelectronic species

Q44.

Isoelectronic species have the same number of valence electrons. Se^{2-}, Br^-, and Rb^+ all have the electron configuration of [Kr]. Thus, the correct answer is **C**.

Difficulty: Medium
Learning Objectives: Bohr's model; Rydberg's equation for hydrogen-like atoms/ions

Q45.

Among the choices, all species are hydrogen-like atoms/ions, which have only one electron. We can apply the Rydberg equation, where R_H is a constant, Z is the atomic number of the atom, n_f and n_i is the energy level of final and initial state, respectively.

$$\Delta E = -R_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

We calculate ΔE for each choice and compare the magnitude.

For choice A, $\Delta E = -R_{\mathrm{H}} 1^2 \left(\frac{1}{4} - \frac{1}{1}\right) = \frac{3}{4} R_H$. For choice B, $\Delta E = -R_{\mathrm{H}} 2^2 \left(\frac{1}{9} - \frac{1}{4}\right) = \frac{5}{9} R_{\mathrm{H}}$. For choice C, $\Delta E = -R_{\mathrm{H}} 3^2 \left(\frac{1}{16} - \frac{1}{9}\right) = \frac{7}{16} R_{\mathrm{H}}$. For choice D, $\Delta E = -R_{\mathrm{H}} 4^2 \left(\frac{1}{25} - \frac{1}{16}\right) = \frac{9}{25} R_{\mathrm{H}}$. Thus, the correct answer is **A**.

Q46.

Difficulty: Easy
Learning Objectives: electron configuration and number of unpaired electrons

The electron configuration of cations is assigned by removing electrons with the greatest principal quantum number. The electron configurations for Fe^{3+}, Co^{3+}, Ni^{3+}, and $Cu^{3+}$are $[Ar]3d^5$, $[Ar]3d^6$, $[Ar]3d^7$, and $[Ar]3d^5$, respectively. By Hund's rule, we can know that $\mathbf{Fe^{3+}}$ has the most unpaired electrons of 5. Thus, the correct answer is **A**.

Q47.

Difficulty: Easy
Learning Objectives: concept of Pauli exclusion principle

The Pauli exclusion principle states that no two electrons in the same atom can have identical values for all four of their quantum numbers. The only thing differentiates two electrons in the same orbital is their spins. Since there are only two possible spins, the atomic orbital can have no more than two electrons. Thus, the correct answer is **C**.

Q48.

Difficulty: Easy
Learning Objectives: types of nuclear decay

During the process of nuclear decay, the mass number (NOT the mass) and charge number keep constant. The reaction of copper-64 positron emission is shown below.

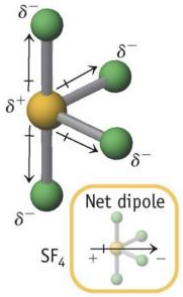
$$^{64}_{29}\mathrm{Cu} = {}^{64}_{28}\mathrm{Ni} + {}^{0}_{1}e$$

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

Q49.

Difficulty: Medium
Learning Objectives: molecular geometry and VSEPR model; polarity of molecules

According to the VSEPR model, the geometry of the four molecules is tetrahedral (CF_4), planar (C_2F_4, $F_2C{=}CF_2$), see-saw (SF_4), and octahedral (SF_6), respectively. The dipole moments of all molecules cancel out except for the asymmetric SF_4 with a see-saw geometry as shown below:



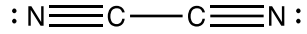
source: to be added

Thus, SF_4 is the only polar compound. The correct answer is **C**.

Difficulty: Easy
Learning Objectives: Lewis structures; concepts of sigma and pi bonds

Q50.

The Lewis structure of cyanogen (NCCN) is shown below:

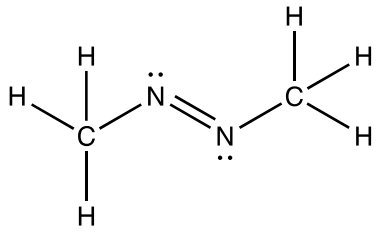


All single bonds are σ bonds, and there are two π bonds in a triple bond and one π bond in a double bond. Thus, there are totally four π bonds in cyanogen. The correct answer is **B**.

Difficulty: Medium
Learning Objectives: Lewis structures; molecular geometry and VSEPR model

Q51.

In this question, we draw the Lewis structure and apply VSEPR model. The Lewis structure of azomethane (CH_3NNCH_3) is shown below.

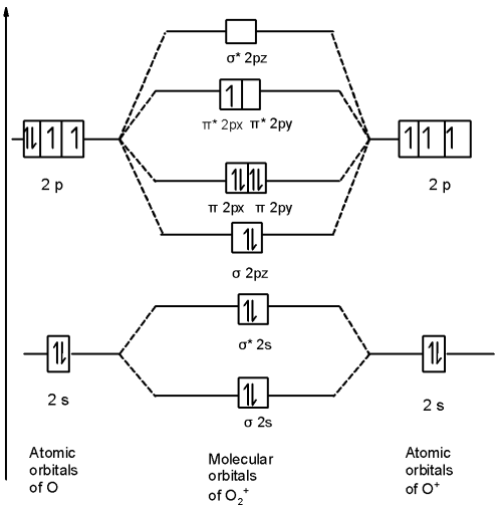


By applying VSEPR model, we can know that the geometry is tetrahedral around each carbon and bent around each nitrogen. Thus, the correct answer is **A**.

Difficulty: Medium
Learning Objectives: molecular orbital diagram; bond order calculation

Q52.

The molecular orbital diagram of O_2^+ is shown as follows.



$$\text{Bond Order} = \frac{\#e^- \text{ of bonding MO} - \#e^- \text{ of antibonding MO}}{2} = \frac{8-3}{2} = 2.5$$

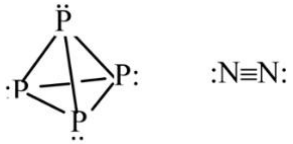
Thus, the correct answer is **D**.

Q53.

Difficulty: Easy

Learning Objectives: uniqueness of second period elements; strengths of pi bonds

Phosphorus forms a weaker π bond than the nitrogen does due to the larger size of phosphorus, which results in a weaker overlap of p orbitals in a phosphorus molecule. Thus, phosphorus prefers the structure with less π bond while nitrogen prefers the structure with more π bonds. The structures of P_4 and N_2 are shown as follows.



:N≡N:

source: Wikipedia

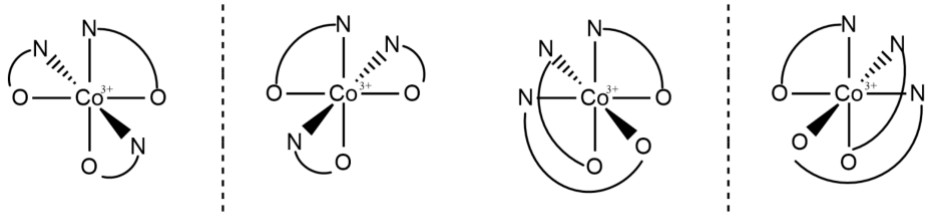
The correct answer is **A**.

Q54.

Difficulty: Hard

Learning Objectives: isomerism of coordination compounds; *fac*/*mer* isomers and enantiomers

In the octahedral complex $Co(NH_2CH_2CO_2)_3$, each glycinate ion $NH_2CH_2CO_2^-$ is a bidentate ligand, which binds to cobalt through its nitrogen atom and one of its oxygen atoms. To simplify the drawing, here we use $\widehat{N\ O}$ to represent the bident ligand. The isomers can be first classified into two categories, meridional and facial, as shown below. In the *mer*- isomers, the three nitrogens (or the three oxygens) are in a row (a meridional semicircle), while they are located on an equilateral triangle in the *fac*- isomers. The next step is to analyze the possible optical isomers. The *mer*- and *fac*- isomers are both chiral without any inversion center or mirror plane in the structures, which means each of them has an enantiomer, the mirror image.



mer - one pair of enantiomers fac - one pair of enantiomers

Therefore, there are four stereoisomers in total, and the correct answer is **B**.

Q55.

Difficulty: Easy

Learning Objectives: double bond equivalence; functional groups

Either alcohol group or ketone group may be contained in the molecule with a formula of $C_5H_{10}O$. Examples are shown below.

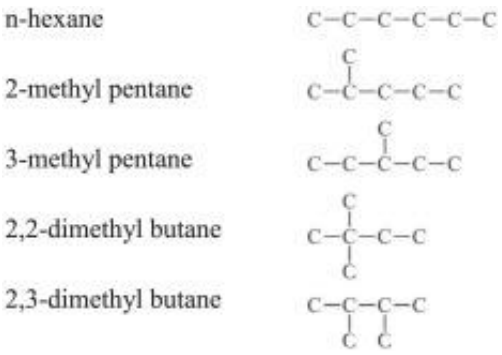
structure of 3-pentanone *structure of cyclopentanol*

There are other reasonable structures with both functional groups, ketone and alcohol as if it includes an oxygen atom and a ring or a double bond to satisfy the double bond equivalence (DBE = 1). Thus, the correct answer is **C**.

Difficulty: Medium
Learning Objectives: isomer counting of alkanes

Q56.

The names and structures of all isomers of C_6H_{14} are shown below:



Except for the *n*-hexane, all other isomers are branched alkanes.

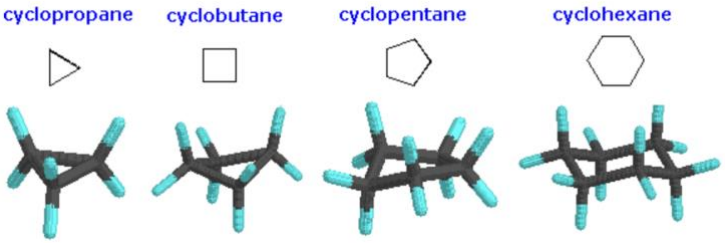
Thus, the correct answer is **D**.

A systematic strategy to draw all isomers of alkanes is to change the number of carbons on the main chain (the longest chain) from the most to the possible least and to add the remaining carbons as branches on different positions.

Difficulty: Medium
Learning Objectives: bond angles of cycloalkanes

Q57.

The C–C–C bond angle in its most stable conformation of cyclopropane, cyclobutane, cyclopentane, and cyclohexane is 60°, ~90°, 109.5°, and 109.5°, respectively, as shown in the structures below:



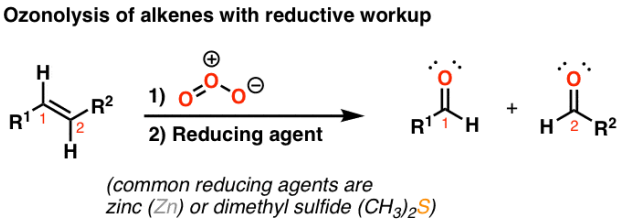
The most stable conformation of cyclohexane is the chair conformation with a bond angle of 109.5°, which is the most different from the value given. Thus, the correct answer is **D**.

As the hybridization of all carbons in all the above cycloalkanes is sp^3, ideally, the carbons are supposed to be tetrahedral with a bong angle of 109.5°. The actual bond angles in cyclopropane and cyclobutene is much smaller than the ideal values, thus, there is a significant *ring string* in those small rings, resulting in unstable structures. The nonplanar structures of the mid-size rings (C5-C7) releases the ring string with ideal bond angle of 109.5°.

Q58.

Difficulty: Medium
Learning Objectives: ozonolysis of alkenes

Among N_2, O_3, N_2O, and NH_3, O_3 is well known to react with the C=C in 1-hexene by ozonolysis, as shown below:



source: masterorganicchemistry

Moreover, N_2O as a 1,3-dipole, can also react with alkenes through a similar mechanism with a slower rate. Thus, the correct answer is ozone, **B**.

Q59.

Difficulty: Hard
Learning Objectives: enantiomers and diastereomers

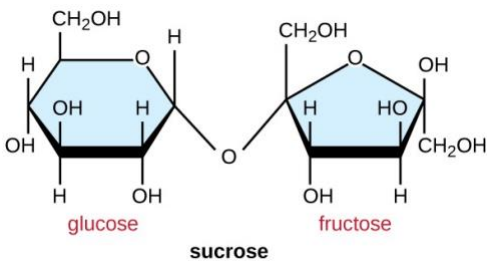
The structure is chiral because we cannot find a mirror plane or an inversion center of the molecule. Structure B is a diastereomer of the given molecule, and structure C is identical as the given molecule. Thus, **A** is the correct answer.

To see the relationship of these molecules clearly, we may need to rotate the molecule through the C2–C3 bond or flip the molecule on the paper. For instance, by flipping the molecule in option A to align the carbon the chain with the target molecule, we can see that both –OH groups have an opposite configuration, which confirms it as the enantiomer. For the molecule in option B, we need to rotate the left part of the molecule though the C2–C3 bond to align the carbon chain, then we can see that left chiral carbon has the same configuration with the target molecule while the right one is the opposite, thus, molecule B is a diastereomer, a stereoisomer which is not an enantiomer. Molecule in option C is represented in Newman projection, which visualizes the conformation of the C2–C3 bond from front to back, with a central dot representing the front atom and a circle representing the back carbon. As the carbon chain is aligned with the target molecule, it is not hard to see both –OH groups are towards up, which makes it identical with the target molecule.

Q60.

Difficulty: Hard
Learning Objectives: functional groups of common biomolecules

The structure of sucrose, which is made by the dehydration a molecule of glucose and a molecular of fructose is shown as follows.



source: to be added

Apparently, it does not contain C=O double bonds. Thus, the correct answer is **A**.

Moreover, glyceryl trioleate in option B is an ester, which includes a C=O in the ester group. Phenylalanine *t*RNA in option C is a nucleic acid, which is made by a five-carbon sugar, a phosphate group, and a nitrogenous base, without looking into the exact structure of each nitrogenous base, we can conclude some of them include C=O with no doubt. Trypsin in option D is a protein, which is a natural polymer of amino acids, which include the carboxylate groups with C=O.