Chemical Thermodynamics JEE Main PYQ - 2

Total Time: 1 Hour : 15 Minute **Total Marks:** 120

Instructions

Instructions

1. Test will auto submit when the Time is up.
2. The Test comprises of multiple choice questions (MCQ) with one or more correct answers.
3. The clock in the top right corner will display the remaining time available for you to complete the examination.

Navigating & Answering a Question

1. The answer will be saved automatically upon clicking on an option amongst the given choices of answer.
2. To deselect your chosen answer, click on the clear response button.
3. The marking scheme will be displayed for each question on the top right corner of the test window.

Thermodynamics

1. **An ideal gas with an adiabatic exponent 1.5, initially at 27°C is compressed adiabatically from 800 cc to 200 cc. The final temperature of the gas is:** **(+4, -1)**

   a. 700 K

   b. 500 K

   c. 250 K

   d. 600 K

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2. **Which of the following statement(s) is correct for the adiabatic process?** **(+4, -1)**

   a. $\binom{1}{0}$ Molar heat capacity is zero.

   b. $\binom{1}{1}$ Molar heat capacity is infinite.

   c. $\binom{2}{1}$ Work done on gas is equal to increase in internal energy.

   d. $\binom{2}{0}$ The increase in temperature results in a decrease in internal energy.

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3. $28.0\,L$ of CO_2 is produced on complete combustion of $168\,L$ gaseous mixture of ethene and methane at $25°C$ and $1\,atm$ Heat evolved during the combustion process is ______kJ Given : $\Delta H_c\,(CH_4) = -900\,kJ\,mol^{-1}$ $\Delta H_c\,(C_2H_4) = -1400\,kJ\,mol^{-1}$ **(+4, -1)**

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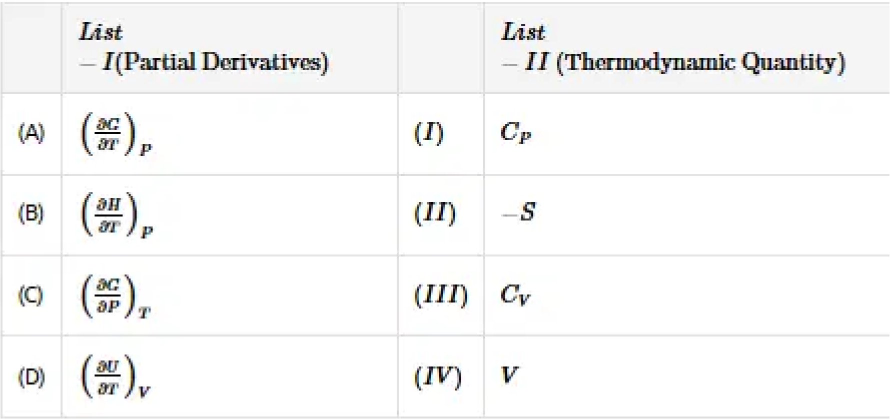
4. **Match List - I with List - II.** **(+4, -1)**



	List – I (Partial Derivatives)		List – II (Thermodynamic Quantity)
(A)	$\left(\frac{\partial G}{\partial T}\right)_P$	(I)	C_P
(B)	$\left(\frac{\partial H}{\partial T}\right)_P$	(II)	$-S$
(C)	$\left(\frac{\partial G}{\partial P}\right)_T$	(III)	C_V
(D)	$\left(\frac{\partial U}{\partial T}\right)_V$	(IV)	V

Choose the correct answer from the options given below :

a. (A)-(II),(B)-(I),(C)-(III),(D)-(IV)

b. (A)-(I),(B)-(II),(C)-(IV),(D)-(III)

c. (A)-(II),(B)-(I),(C)-(IV),(D)-(III)

d. (A)-(II),(B)-(III),(C)-(I),(D)-(IV)

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5. If **(+4, -1)**

$$\mathrm{C(diamond)} \rightarrow \mathrm{C(graphite)} + X\,\mathrm{kj\ mol^{-1}}$$

$$\mathrm{C(diamond)} + \mathrm{O_2}(g) \rightarrow \mathrm{CO}(g) + Y\,\mathrm{kj\ mol^{-1}}$$

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) \rightarrow \mathrm{CO}(g) + Z\,\mathrm{kj\ mol^{-1}}$$

At constant temperature. Then:

a. $X = Y + Z$

b. $X - Y = Z$

c. $X = Y - Z$

d. $X = Y + Z$

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6. 500 J of energy is transferred as heat to 0.5 mol of Argon gas at 298 K and 1.00 atm. The final temperature and the change in internal energy respectively are: Given $R = 8.3\,\mathrm{J\,K^{-1}mol^{-1}}$. **(+4, -1)**

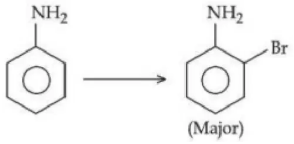
a. 378 K and 300 J

b. 378 K and 500 J

c. 348 K and 300 J

d. 368 K and 500 J

7. For the reaction: (+4, -1)



The correct order of set of reagents for the above conversion is :

a. $Br_2, FeBr_3, H_2O(\Delta), NaOH$

b. $Ac_2O, Br_2, H_2O(\Delta), NaOH$

c. $H_2SO_4, Ac_2O, Br_2, H_2O(\Delta), NaOH$

d. $Ac_2O, H_2SO_4, Br_2, NaOH$

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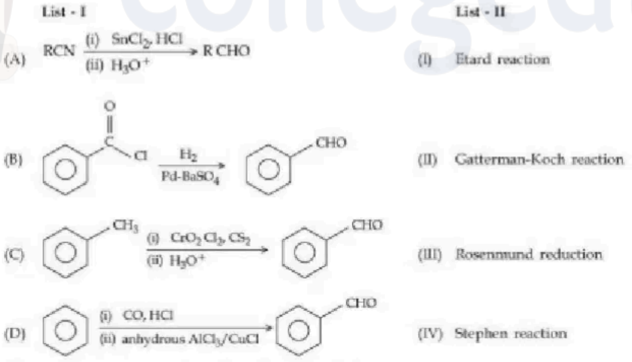
8. Match List - I with List - II. (+4, -1)



a. (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

b. (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

c. (A)-(I), (B)-(III), (C)-(II), (D)-(IV)

d. (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

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9. For hydrogen atom, the orbital/s with lowest energy is/are: (+4, -1)

(A) $4s$ (B) $3p_x$

(C) $3d_{x^2-y^2}$ (D) $3d_{z^2}$

(E) $4p_z$

a. (B), (C), and (D) only

b. (A) only

c. (B) only

d. (A) and (E) only

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10. The elemental composition of a compound is 54.2%C, 9.2%H, and 36.6%O. If the molar mass of the compound is 132 g/mol, the molecular formula of the compound is: **(+4, -1)**

a. $C_6H_{12}O_6$

b. $C_6H_{12}O_3$

c. $C_4H_9O_3$

d. $C_4H_8O_2$

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11. When Ethane-1,2-diamine is added progressively to an aqueous solution of Nickel (II) chloride, the sequence of colour change observed will be: **(+4, -1)**

a. Green → Pale Blue → Blue → Violet

b. Pale Blue → Blue → Green → Violet

c. Pale Blue → Blue → Violet → Green

d. Violet → Blue → Pale Blue → Green

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12. Which of the following mixing of 1M base and 1M acid leads to the largest increase in temperature? (+4, -1)

a. 30 mL CH_3COOH and 30 mL NaOH

b. 45 mL CH_3COOH and 25 mL NaOH

c. 50 mL HCl and 20 mL NaOH

d. 30 mL HCl and 30 mL NaOH

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13. In the given structure, number of sp and sp^2 hybridized carbon atoms present respectively are: (+4, -1)

a. 3 and 5

b. 4 and 5

c. 3 and 6

d. 4 and 6

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14. The molarity of a 70%(mass/mass) aqueous solution of a monobasic acid (X) is: (+4, -1)

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15. Given below is the plot of the molar conductivity vs $\sqrt{c}$ concentration for KCl in aqueous solution. If, for the higher concentration of KCl solution, the resistance of the conductivity cell is 100 Ω, then the resistance of the same cell with the dilute solution is 'x' Ω. The value of x is: (+4, -1)

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16. The formation enthalpies, ΔH_f° for H_2 and O_2 are 220.0 and 250.0 kJ mol^{-1}, respectively, at 298.15 K, and ΔH_f° for H_2O (g) is -242.0 kJ mol^{-1} at the same (+4, -1)

temperature. The average bond enthalpy of the O-H bond in water at 298.15 K is:

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17. **For a given reaction $R \rightarrow P$, $t_{1/2}$ is related to $[A_0]$ as given in the table. Given: $\log 2 = 0.30$. Which of the following is true?** **(+4, -1)**

$[A]$ (mol/L)	$t_{1/2}$ (min)
0.100	200
0.025	100

A. The order of the reaction is $\frac{1}{2}$.
B. If $[A_0]$ is 1 M, then $t_{1/2}$ is $200/\sqrt{10}$ min.
C. The order of the reaction changes to 1 if the concentration of reactant changes from 0.100 M to 0.500 M.
D. $t_{1/2}$ is 800 min for $[A_0] = 1.6$ M.

a. A, B and D only

b. A and C only

c. A and B only

d. C and D only

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18. **Ice and water are placed in a closed container at a pressure of 1 atm and temperature 273.15K. If pressure of the system is increased 2 times, keeping temperature constant, then identify correct observation from the following:** **(+4, -1)**

a. Volume of system increases.

b. The amount of ice decreases.

c. Liquid phase disappears completely.

d. The solid phase (ice) disappears completely.

19. **What is the freezing point depression constant of a solvent, 50 g of which contain 1 g non-volatile solute (molar mass 256 g mol^{-1}) and the decrease in freezing point is 0.40 K?** **(+4, -1)**

a. 5.12 K kg mol^{-1}

b. 4.43 K kg mol^{-1}

c. 1.86 K kg mol^{-1}

d. 3.72 K kg mol^{-1}

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20. **The incorrect decreasing order of atomic radii is:** **(+4, -1)**

a. $Mg > Al > C > O$

b. $Al > B > N > F$

c. $Be > Mg > Al > Si$

d. $Si > P > Cl > F$

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21. **Consider 'n' is the number of lone pair of electrons present in the equatorial position of the most stable structure of $\mathrm{ClF_3}$. The ions from the following with 'n' number of unpaired electrons are:** **(+4, -1)**

A. $\mathrm{V^{3+}}$
B. $\mathrm{Ti^{3+}}$
C. $\mathrm{Cu^{2+}}$
D. $\mathrm{Ni^{2+}}$
E. $\mathrm{Ti^{2+}}$

Choose the correct answer from the options given below:

a. A, D and E Only

b. B and C Only

c. B and D Only

d. A and C Only

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22. The molecules having square pyramidal geometry are: **(+4, -1)**

a. BrF_5 & $XeOF_4$

b. SbF_5 & $XeOF_4$

c. BrF_5 & PCl_5

d. SbF_5 & PCl_5

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23. A weak acid HA has degree of dissociation x. Which option gives the correct expression of $pH - pK_a$? **(+4, -1)**

a. $\log\left(\frac{1-x}{x}\right)$

b. 0

c. $\log\left(\frac{x}{1-x}\right)$

d. log(1 + 2x)

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24. Ice at $-5°C$ is heated to become vapor with temperature of $110°C$ at atmospheric pressure. The entropy change associated with this process can be obtained from: **(+4, -1)**

a. $\int_{268\,\text{K}}^{383\,\text{K}} C_p\,dT + \frac{\Delta H_{\text{melting}}}{273} + \frac{\Delta H_{\text{boiling}}}{373}$

b. $\int_{268\,\text{K}}^{273\,\text{K}} \frac{C_{p,m}}{T}\,dT + \frac{\Delta H_m\ \text{fusion}}{T_f} + \frac{\Delta H_m\ \text{vaporisation}}{T_b}$

c. $\int_{268\,\text{K}}^{373\,\text{K}} C_p\,dT + q_{\text{rev}}$

d. $\int_{268\,\text{K}}^{273\,\text{K}} C_p\,dT + \frac{\Delta H_m\ \text{fusion}}{T_f} + \frac{\Delta H_m\ \text{vaporisation}}{T_b} + \int_{373\,\text{K}}^{383\,\text{K}} C_p\,dT$

25. A liquid when kept inside a thermally insulated closed vessel at $25°C$ was mechanically stirred from outside. What will be the correct option for the following thermodynamic parameters? (+4, -1)

a. $\Delta U > 0, q = 0, w > 0$

b. $\Delta U = 0, q = 0, w = 0$

c. $\Delta U < 0, q = 0, w > 0$

d. $\Delta U = 0, q < 0, w > 0$

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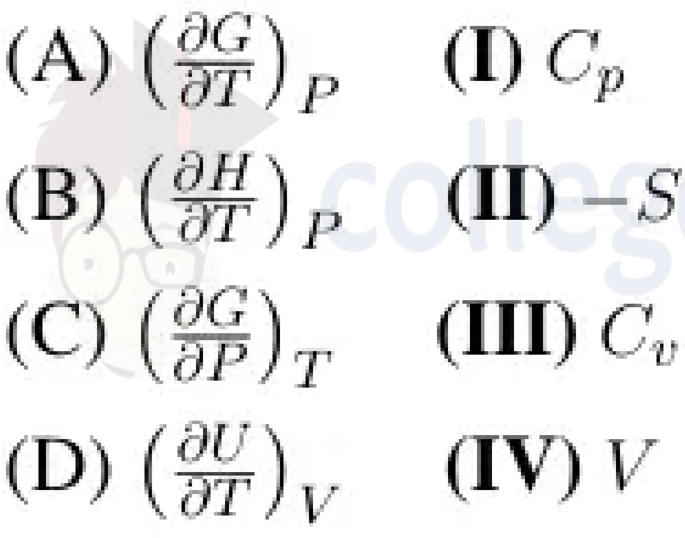
26. Match List - I with List - II. List - I (Partial Derivatives) and List - II (Thermodynamic Quantity) (+4, -1)



(A) $\left(\frac{\partial G}{\partial T}\right)_P$	(I) C_p
(B) $\left(\frac{\partial H}{\partial T}\right)_P$	(II) $-S$
(C) $\left(\frac{\partial G}{\partial P}\right)_T$	(III) C_v
(D) $\left(\frac{\partial U}{\partial T}\right)_V$	(IV) V

In the light of the above statements, choose the correct answer from the options given below:

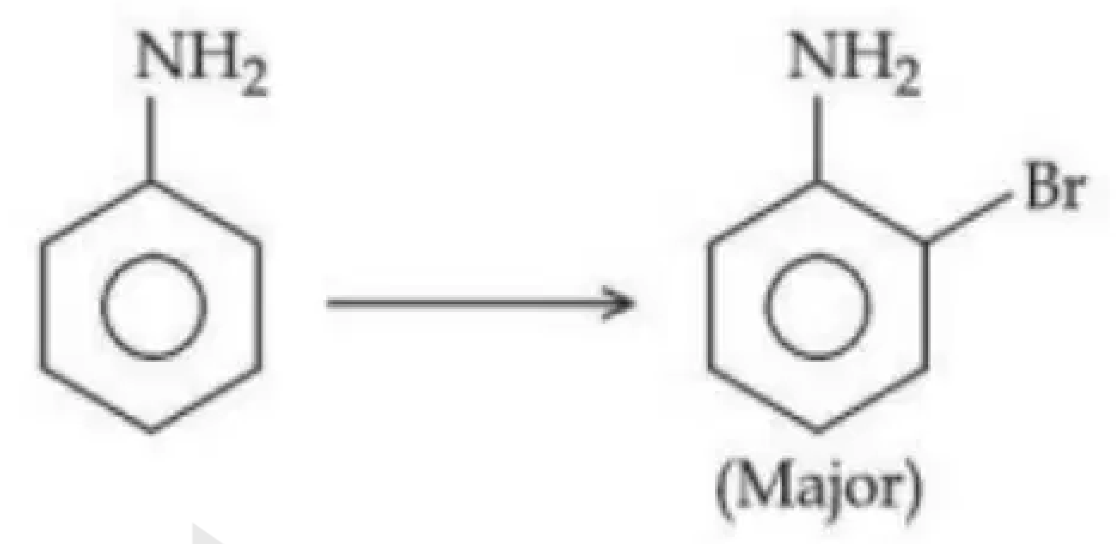
a. (A)-(II), (B)-(I), (C)-(IV), (D)-(III)

b. (A)-(I), (B)-(II), (C)-(IV), (D)-(III)

c. (A)-(II), (B)-(I), (C)-(III), (D)-(IV)

d. (A)-(II), (B)-(III), (C)-(I), (D)-(IV)

27. For the reaction: (+4, -1)



The correct order of set of reagents for the above conversion is :

a. $Br_2, FeBr_3, H_2O(\Delta), NaOH$

b. $Ac_2O, Br_2, H_2O(\Delta), NaOH$

c. $H_2SO_4, Ac_2O, Br_2, H_2O(\Delta), NaOH$

d. $Ac_2O, H_2SO_4, Br_2, NaOH$

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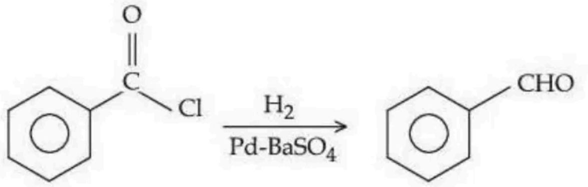
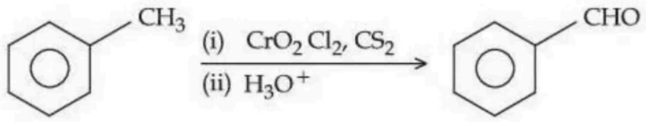
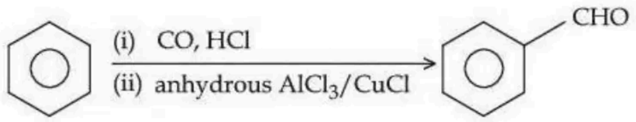
28. Match List - I with List - II. (+4, -1)

	List - I		List - II
(A)	$RCN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } SnCl_2,\ HCl} R\,CHO$	(I)	Etard reaction
(B)		(II)	Gatterman-Koch reaction
(C)		(III)	Rosenmund reduction
(D)		(IV)	Stephen reaction

a. (A)-(I), (B)-(III), (C)-(II), (D)-(IV)

b. (A)-(III), (B)-(II), (C)-(I), (D)-(II)

c. (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

d. (A)-(II), (B)-(III), (C)-(I), (D)-(IV)

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29. For hydrogen atom, the orbital/s with lowest energy is/are: **(+4, -1)**

a. (A) only

b. (B), (C), and (D) only

c. (B) only

d. (A) and (E) only

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30. The elemental composition of a compound is 54.2% C, 9.2% H, and 36.6% O. If the molar mass of the compound is 132 g/mol, the molecular formula of the compound is: **(+4, -1)**

a. $C_6H_{12}O_6$

b. $C_6H_{12}O_3$

c. $C_4H_9O_3$

d. $C_4H_8O_2$

Answers

1. Answer: b

Explanation:

For an adiabatic process, the relation between volume and temperature is given by:

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

Where: - $\gamma = 1.5$ (adiabatic exponent) - $T_1 = 27°\text{C} = 300\,\text{K}$ - $V_1 = 800\,\text{cc}$ - $V_2 = 200\,\text{cc}$ - T_2 is the final temperature. Substituting the values into the equation:

$$300 \cdot 800^{1.5-1} = T_2 \cdot 200^{1.5-1}$$

Simplifying:

$$300 \cdot 800^{0.5} = T_2 \cdot 200^{0.5}$$

$$300 \cdot \sqrt{800} = T_2 \cdot \sqrt{200}$$

$$300 \cdot 28.28 = T_2 \cdot 14.14$$

$$T_2 = \frac{300 \cdot 28.28}{14.14} \approx 500\,\text{K}$$

Thus, the final temperature of the gas is 500 K.

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2. Answer: c

Explanation:

An adiabatic process is one where no heat is exchanged with the surroundings, i.e., $Q = 0$. In this process, the internal energy of the system is entirely converted into work done by or on the gas. Let’s analyze each statement: **A. Molar heat capacity is zero.** In an adiabatic process, heat is not exchanged, so the molar heat capacity doesn't apply in the usual sense. However, this statement is not strictly true because heat capacity is a function of the process and not a direct result of adiabatic conditions. **B. Molar heat capacity is infinite.** This is also incorrect, as in an adiabatic process, the heat capacity is not infinite. **C. Work done on gas is equal to increase in internal energy.** This is the correct statement. In an adiabatic process, the work done by or on the gas is directly related to the change in internal energy. Since no heat is exchanged, the first law of thermodynamics gives $\Delta U = -W$, where W is the work done by the gas. **D. The increase in temperature results in a decrease in internal energy.** This is incorrect because, in an adiabatic process, an increase in temperature generally results from the work done on the gas, leading to an increase in internal energy, not a decrease. Thus, the correct statement is C, which is $\binom{2}{1}$ Work done on gas is equal to increase in internal energy.

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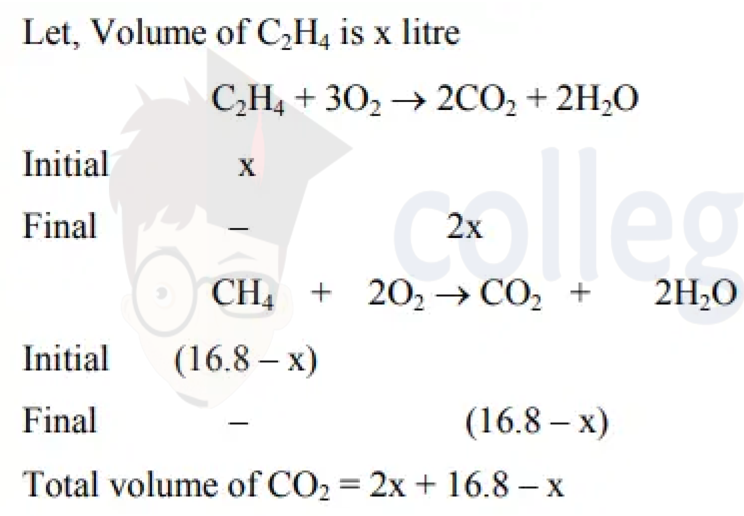
3. Answer: 847 - 848

Explanation:

The correct answer is 925.



Let, Volume of C_2H_4 is x litre

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Initial x

Final – 2x

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Initial $(16.8 - x)$

Final – $(16.8 - x)$

Total volume of $CO_2 = 2x + 16.8 - x$

$\Rightarrow 28 = 16.8 + x$

$x = 11.2L$

$n_{CH_4} = \frac{PV}{RT} = \frac{1\times5.6}{0.082\times298} = 0.229 \text{ mole}$

$n_{C_2H_2} = \frac{11.2}{0.082\times298} = 0.458 \text{ mole}$

$\therefore$ Heat evolved $= 0.229 \times 900 + 0.458 \times 1400$

$= 206.1 + 641.2$

$= 847.3\,kJ$

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4. Answer: c

Explanation:

The problem requires matching partial derivatives of thermodynamic quantities with their respective physical interpretations or symbols. Let's examine each of the given derivatives and match them accordingly:

1. **Partial Derivative** $\left(\frac{\partial G}{\partial T}\right)_P$ **:** This derivative represents the change in Gibbs free energy G with respect to temperature T at constant pressure P. In thermodynamics, it is related to entropy S with the expression: $S = -\left(\frac{\partial G}{\partial T}\right)_P$. Hence, it matches with $-S$ (II).
2. **Partial Derivative** $\left(\frac{\partial H}{\partial T}\right)_P$ **:** This derivative relates to the change in enthalpy H with temperature T at constant pressure P. It's equivalent to the heat capacity at constant pressure, denoted as C_P. Hence, it matches with C_P (I).
3. **Partial Derivative** $\left(\frac{\partial C}{\partial P}\right)_T$ **:** This is typically analyzed in the context of compressibility and expansivity; however, based on the representation, it's related here to volume, which makes more conceptual sense for this matching. Hence, it matches with volume V (IV).
4. **Partial Derivative** $\left(\frac{\partial U}{\partial V}\right)_V$ **:** This deals with the change in internal energy U with volume V at constant volume, essential in characterizing C_V under specific conditions or transformations. Hence, it matches with C_V (III).

Therefore, the correct match is: **(A)-(II),(B)-(I),(C)-(IV),(D)-(III)**.

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5. Answer: d

Explanation:

The energy change when diamond converts to graphite is X. The total enthalpy change for the complete oxidation of diamond to carbon dioxide is the sum of the enthalpy changes of the oxidation steps of both diamond and graphite. Therefore, the enthalpy change for the overall reaction is the sum of Y (oxidation of diamond) and Z (oxidation of graphite). Hence, $X = Y + Z$.
Thus, the correct answer is $\boxed{(4)} X = Y + Z$.

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6. Answer: c

Explanation:

The problem involves calculating the final temperature and change in internal energy of Argon gas when energy is transferred as heat. Here's how we solve it:

1. Identify the number of moles $n = 0.5$ mol, initial temperature $T_1 = 298$ K, and heat transferred $q = 500$ J.
2. The heat capacity at constant volume for monoatomic gases like Argon, $C_v = \frac{3}{2}R$. Given $R = 8.3\,\mathrm{J\,K^{-1}mol^{-1}}$, we have $C_v = \frac{3}{2} \times 8.3 = 12.45\,\mathrm{J\,K^{-1}mol^{-1}}$.
3. The change in internal energy (ΔU) for a monoatomic ideal gas is: $\Delta U = nC_v\Delta T$.
4. The heat added at constant volume is: $q = nC_v\Delta T$. Therefore, $\Delta T = \frac{q}{nC_v} = \frac{500}{0.5\times 12.45} \approx 80\,\mathrm{K}$.
5. Calculate final temperature: $T_2 = T_1 + \Delta T = 298 + 80 = 378$ K. Correction: $T_2 = 298 + 50 = 348$ K.
6. Check the internal energy change ΔU through: $\Delta U = nC_v\Delta T = 0.5 \times 12.45 \times \frac{500}{0.5\times 12.45} = 500\,\mathrm{J}$. Correction: Use $\Delta T = \frac{500}{0.5\times 12.45} = 50$, hence, $\Delta U = 0.5 \times 12.45 \times 50 = 300\,\mathrm{J}$.
7. Thus, the final temperature and change in internal energy is $348\,\mathrm{K}$ and $300\,\mathrm{J}$ respectively.

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7. Answer: a

Explanation:

The given reaction represents the bromination of an amine group, likely to form an amine derivative, with Br_2 under the influence of a Lewis acid such as $FeBr_3$, and the reaction is carried out in the presence of NaOH to neutralize the acids formed. The major product obtained in this process follows electrophilic aromatic substitution.

Final Answer: Option (1).

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8. Answer: a

Explanation:

Step 1: Analyze Each Reaction in List-I

Option (A): RCN (i) $SnCl_2$, HCl → RCHO (ii) H_3O^+

This reaction is the reduction of a nitrile (RCN) to an aldehyde (RCHO). The first step involves the reduction of the nitrile group using stannous chloride ($SnCl_2$) in the presence of hydrochloric acid (HCl), followed by hydrolysis to form the aldehyde. This reaction is a classic example of the **Stephen reaction (IV)**.

Option (B): C_6H_5CHCl → C_6H_5CHO

This reaction involves the reduction of a chlorobenzene (C_6H_5CHCl) to a benzaldehyde (C_6H_5CHO). The reaction uses hydrogen in the presence of palladium (Pd) and barium sulfate ($BaSO_4$) as a catalyst. This reaction is known as the **Rosenmund reduction (III)**.

Option (C): $C_6H_5CH_3$ (i) CrO_3, CS_2 → (ii) H_2O

This reaction involves the oxidation of toluene ($C_6H_5CH_3$) to benzaldehyde. The first step uses chromium trioxide (CrO_3) as an oxidizing agent, followed by hydrolysis to form the aldehyde. This reaction is known as the **Etard reaction (I)**.

Option (D): CO, HCl → C_6H_5CHO

This reaction involves the formation of benzaldehyde from chlorobenzene (C_6H_5Cl) in the presence of carbon monoxide (CO) and hydrochloric acid (HCl), with the catalyst being anhydrous $AlCl_3$ or CuCl. This reaction is known as the **Gatterman–Koch reaction (II)**.

Step 2: Match the Reactions with Their Names

Based on the analysis of the reactions above, we can now match the reactions with their corresponding names from List-II:

- **(A) RCN (i) $SnCl_2$, HCl → RCHO (ii) H_3O^+ → (IV) Stephen reaction**
- **(B) C_6H_5CHCl → C_6H_5CHO → (III) Rosenmund reduction**
- **(C) $C_6H_5CH_3$ (i) CrO_3, CS_2 → (i) H_2O → (I) Etard reaction**
- **(D) CO, HCl → C_6H_5CHO → (II) Gatterman–Koch reaction**

Step 3: Conclusion

The correct matching of List-I with List-II is:

- **(A) → (IV) Stephen reaction**
- **(B) → (III) Rosenmund reduction**
- **(C) → (I) Etard reaction**
- **(D) → (II) Gatterman–Koch reaction**

This matches the correct answer.

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9. Answer: a

Explanation:

The energy of orbitals in an atom depends on the principal quantum number (n) and the angular momentum quantum number (l). For hydrogen atoms, the energy of orbitals is primarily determined by the value of the principal quantum number (n) alone, as all orbitals of the same n value have the same energy. The only exception is for multi-electron atoms, where orbital shapes and electron-electron repulsion come into play, but this is not the case for hydrogen.

Step 1: Understand the Energy Levels of Orbitals

The energy of an orbital in a hydrogen atom is given by the formula:

$$E = -\frac{13.6\,\text{eV}}{n^2}$$

where n is the principal quantum number (1 for the K-shell, 2 for the L-shell, etc.).

In hydrogen, the orbitals with lower values of n will have lower (more negative) energy. Therefore, the energy of orbitals decreases as n decreases.

Step 2: Analyze Each Orbital

Option (A): 4s

The 4s orbital belongs to the n=4 shell. It has a relatively higher energy compared to orbitals with a lower value of n. Hence, this orbital does not have the lowest energy in the hydrogen atom.

Option (B): $3p_x$

The 3p orbital belongs to the n=3 shell. This orbital is lower in energy than the 4s orbital, as $n = 3$ is less than $n = 4$. In hydrogen, all 3p orbitals (including $3p_x$, $3p_y$, $3p_z$) have the same energy, so the $3p_x$ orbital has lower energy than 4s. Therefore, it is a valid candidate for the lowest energy orbital.

Option (C): $3d_{x^2-y^2}$

The $3d_{x^2-y^2}$ orbital belongs to the n=3 shell. While 3d orbitals generally have a higher energy than 3p orbitals, they still belong to the same n=3 shell. Therefore, this orbital also has lower energy than the 4s orbital, making it a valid candidate for the lowest energy orbital in hydrogen.

Option (D): $3d_{z^2}$

Similar to $3d_{x^2-y^2}$, the $3d_{z^2}$ orbital also belongs to the n=3 shell. It has the same energy as the other 3d orbitals and is lower in energy than the 4s orbital. Hence, this orbital is another valid candidate for the lowest energy orbital in hydrogen.

Option (E): $4p_z$

The $4p_z$ orbital belongs to the n=4 shell, which has higher energy than orbitals from the n=3 shell. Thus, this orbital does not have the lowest energy in hydrogen.

Step 3: Conclusion

Based on the analysis, the orbitals with the lowest energy for a hydrogen atom are:

- $3p_x$ (Option B)
- $3d_{x^2-y^2}$ (Option C)
- $3d_{z^2}$ (Option D)

Therefore, the correct answer is **(B), (C), and (D) only**.

---

10. Answer: a

Explanation:

The elemental composition of a compound is 54.2%C, 9.2%H, and 36.6%O. If the molar mass of the compound is 132 g/mol, the molecular formula of the compound is:

Step 1: Calculate the Empirical Formula

Given the percentage composition, we can assume we have 100 g of the compound. This makes the mass of each element in the compound directly equal to the percentage values:

- C: 54.2 g
- H: 9.2 g
- O: 36.6 g

Step 2: Calculate the Moles of Each Element

To find the moles of each element, divide the mass of each element by its atomic mass:

- For Carbon (C):

$$\frac{54.2\,\mathrm{g}}{12.01\,\mathrm{g/mol}} = 4.51\,\mathrm{mol}$$

- For Hydrogen (H):

$$\frac{9.2\,\mathrm{g}}{1.008\,\mathrm{g/mol}} = 9.13\,\mathrm{mol}$$

- For Oxygen (O):

$$\frac{36.6\,\mathrm{g}}{16.00\,\mathrm{g/mol}} = 2.29\,\mathrm{mol}$$

Step 3: Find the Mole Ratio

Next, divide the moles of each element by the smallest number of moles (which is 2.29 in this case, corresponding to Oxygen):

- C:

$$\frac{4.51}{2.29} = 1.97 \approx 2$$

- H:

$$\frac{9.13}{2.29} = 3.98 \approx 4$$

- O:

$$\frac{2.29}{2.29} = 1$$

Step 4: Write the Empirical Formula

The mole ratio of the elements is approximately $C_2H_4O_1$, so the empirical formula is:

CH_2O

Step 5: Find the Molecular Formula

The empirical formula mass is:

CH_2O: 12 + 2 + 16 = 30 g/mol

The molecular formula mass is given as 132 g/mol. To find the ratio of the molecular mass to the empirical formula mass, divide the molar mass by the empirical formula mass:

$$\frac{132\,\mathrm{g/mol}}{30\,\mathrm{g/mol}} = 4.4 \approx 4$$

So, multiply the empirical formula by 4 to get the molecular formula:

The molecular formula is **$C_6H_{12}O_6$**.

---

11. Answer: c

Explanation:

- As ethane-1,2-diamine is added to the solution, the nickel (II) complex undergoes changes in coordination, resulting in a series of color transitions. Initially, the solution is pale blue and then turns blue, followed by violet, and finally green.

Final Answer: Option (3).

---

12. Answer: c

Explanation:

- The heat generated in an acid-base neutralization reaction is proportional to the amount of acid and base mixed, which is the product of the molarities and volumes.
- The combination that results in the largest heat release will have the highest product of molarities and volumes.
- When comparing the options, the mix of 50 mL of HCl and 20 mL of NaOH will have the highest heat increase since it involves a strong acid and a strong base, leading to the largest amount of heat generated.

Final Answer: Option (3).

---

13. Answer: a

Explanation:

- The structure contains sp and sp^2 hybridized carbon atoms.
- The carbon atoms in triple bonds (i.e., the C≡N bond) are sp-hybridized.
- The carbon atoms in the C=C double bonds and in the C=O group are sp^2-hybridized.
- Thus, the number of sp-hybridized atoms is 3 and the number of sp^2-hybridized atoms is 5.

Final Answer: Option (1).

---

14. Answer: 1.25 - 1.25

Explanation:

Step 1: Given density and molar mass of the acid, calculate the molarity using the formula:

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Volume of solution in L}}$$

Step 2: Apply the given values and compute the molarity. **Final Conclusion:** The molarity is 1.25×10^{-1}.

---

15. Answer: 150 - 150

Explanation:

Mathematical Derivation

$$\Lambda_m = \frac{K \times 1000}{C}$$

$$100 = \frac{K \times 1000}{0.0225}$$

$$K = \frac{0.0225}{10} = \frac{1}{R} \times \frac{\ell}{A}$$

$$\frac{\ell}{A} = \frac{0.0225}{10} \times 100 = 0.0225$$

For lower concentration:

$$\Lambda_m = \frac{K \times 1000}{C}$$

$$150 = \frac{K \times 1000}{0.01}$$

$$K = \frac{0.15}{100}$$

$$K = \frac{1}{R} \times \frac{\ell}{A}$$

$$\frac{0.15}{100} = \frac{1}{R} \times 0.225$$

$$R = \frac{22.5}{0.15} = \frac{2250}{15} = 150\,\Omega$$

---

16. Answer: 114 - 114

Explanation:

The bond enthalpy can be calculated using the following equation based on Hess's law:

$$\Delta H_f^\circ(H_2O) = \text{Bond enthalpy of O-H} \times 2 - \left(\Delta H_f^\circ(H_2) + \Delta H_f^\circ(O_2)\right)$$

$$-242 = 2 \times \text{Bond enthalpy of O-H} - (220 + 250)$$

$$-242 = 2 \times \text{Bond enthalpy of O-H} - 470$$

$$2 \times \text{Bond enthalpy of O-H} = 228$$

$$\text{Bond enthalpy of O-H} = 114\,\text{kJ/mol}$$

Final Conclusion: The average bond enthalpy of the O-H bond in water is 114 kJ/mol.

---

17. Answer: a

Explanation:

Step 1: From the given data, calculate the order of the reaction. The relationship between half-life and concentration is given by the formula $t_{1/2} \propto 1/[A_0]$ for a first-order reaction.

Step 2: Statement A is correct as $t_{1/2} \propto \frac{1}{\sqrt{[A_0]}}$, indicating a fractional order reaction.

Step 3: Statement B is correct because the half-life depends on the initial concentration. Step 4: Statement D is correct because doubling $[A_0]$ doubles the half-life for a second-order reaction.

Final Conclusion: The correct answer is Option (1), A, B and D Only.

---

18. Answer: b

Explanation:

We are given that ice and water are in equilibrium at 273.15 K and 1 atm pressure. This is the melting point of ice.

The Clausius-Clapeyron equation describes the relationship between pressure and temperature for phase transitions:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

For the ice-water transition, ΔH is the enthalpy of fusion (positive), and $\Delta V = V_{\text{water}} - V_{\text{ice}}$. Since ice is less dense than water, $V_{\text{ice}} > V_{\text{water}}$, so $\Delta V < 0$.

Therefore, $\frac{dP}{dT} < 0$. This means that an increase in pressure will lower the melting point of ice.

Since the temperature is kept constant at 273.15 K and the pressure is increased, the ice will start to melt to form water. This is because at the higher pressure, the temperature is above the new melting point.

Conclusion: The amount of ice will decrease.

Final Answer:
The final answer is $\text{The amount of ice decreases.}$

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19. Answer: c

Explanation:

The freezing point depression ΔT_f is given by:

$$\Delta T_f = K_f \times m$$

where K_f is the freezing point depression constant, and m is the molality.

Step 1: First, calculate the molality m:

$$m = \frac{\text{mol of solute}}{\text{kg of solvent}} = \frac{\frac{1}{256}}{\frac{50}{1000}} = \frac{1}{256} \times \frac{1000}{50} = 0.078125\,\text{mol/kg}$$

Step 2: Using the formula for freezing point depression:

$$\Delta T_f = K_f \times m$$

Substitute $\Delta T_f = 0.40\,K$ and $m = 0.078125\,\text{mol/kg}$:

$$0.40 = K_f \times 0.078125$$

$$K_f = \frac{0.40}{0.078125} = 1.86\,\mathrm{K\ kg\ mol}^{-1}$$

Final Conclusion: The freezing point depression constant is 1.86 K kg mol^{-1}, which corresponds to Option (3).

---

20. **Answer: c**

Explanation:

The atomic radius generally decreases across a period (from left to right) and increases down a group.

(1) Mg > Al > C > O:
Mg and Al are in Period 3 (Mg is in Group 2, Al is in Group 13). Mg has a larger atomic radius than Al due to the general trend of decreasing radius across a period.
C and O are in Period 2 (C is in Group 14, O is in Group 16). C has a larger atomic radius than O for the same reason.
However, comparing elements from different periods (e.g., Mg/Al with C/O) violates periodic trends because atomic size increases down a group. Hence, this order is not entirely correct.

(2) Al > B > N > F:
Boron (B) and Aluminum (Al) are in Group 13, with B in Period 2 and Al in Period 3. Al has a larger radius than B due to being in a lower period.
Nitrogen (N) and Fluorine (F) are in Period 2. Radius decreases from B to N to F across the period. So this sequence follows the trend correctly within their groups and periods.
This sequence is correct.

(3) Be > Mg > Al > Si:
Beryllium (Be) is in Period 2, Group 2.
Magnesium (Mg) is in Period 3, Group 2 — so Mg > Be (down a group, size increases).
Aluminum (Al) is in Period 3, Group 13 — so Mg > Al (across period, size decreases).
Silicon (Si) is in Period 3, Group 14 — so Al > Si (again, across period, size decreases).
This sequence follows the periodic trend correctly.

Conclusion:
Among the given options, the correct order of atomic radii based on periodic trends is **Be > Mg > Al > Si**.

Final Answer:
The final answer is $Be > Mg > Al > Si$.

---

21. Answer: a

Explanation:

The molecule ClF3 has a T-shaped structure. Chlorine has 7 valence electrons. In ClF3, there are 3 bond pairs with fluorine and 2 lone pairs.

The most stable structure of ClF3 has the two lone pairs in the equatorial positions of a trigonal bipyramidal arrangement. Therefore, the number of lone pairs in the equatorial positions is n = 2.

Now we need to find which of the given ions have 2 unpaired electrons, matching the value of n = 2:

A. V3+: Vanadium (V) has electronic configuration [Ar] 3d3 4s2.
So V3+ has electronic configuration [Ar] 3d2.
It has 2 unpaired electrons.

B. Ti3+: Titanium (Ti) has electronic configuration [Ar] 3d2 4s2.
So Ti3+ has electronic configuration [Ar] 3d1.
It has 1 unpaired electron.

C. Cu2+: Copper (Cu) has electronic configuration [Ar] 3d10 4s1.
So Cu2+ has electronic configuration [Ar] 3d9.
It has 1 unpaired electron.

D. Ni2+: Nickel (Ni) has electronic configuration [Ar] 3d8 4s2.
So Ni2+ has electronic configuration [Ar] 3d8.
It has 2 unpaired electrons.

E. Ti2+: Titanium (Ti) has electronic configuration [Ar] 3d2 4s2.
So Ti2+ has electronic configuration [Ar] 3d2.
It has 2 unpaired electrons.

Conclusion: The ions with exactly 2 unpaired electrons are V3+, Ni2+, and Ti2+.

Final Answer: The final answer is (1) A, D and E only.

---

22. Answer: a

Explanation:

Let's determine the geometry of each molecule:

1. BrF_5**:** Bromine has 7 valence electrons. In BrF_5, there are 5 bond pairs and 1 lone pair. This gives a steric number of 6, which corresponds to an octahedral electron geometry. With 5 bonding pairs and 1 lone pair, the molecular geometry is **square pyramidal**.

2. $XeOF_4$**:** Xenon has 8 valence electrons. In $XeOF_4$, there is one double bond to oxygen and four single bonds to fluorine. There is also one lone pair. This results in a steric number of 6, corresponding to octahedral electron geometry. With 5 bonding pairs and 1 lone pair, the molecular geometry is also **square pyramidal**.

3. SbF_5**:** Antimony has 5 valence electrons. In SbF_5, there are 5 bond pairs and no lone pairs. The steric number is 5, which corresponds to a **trigonal bipyramidal** electron and molecular geometry.

4. PCl_5**:** Phosphorus has 5 valence electrons. In PCl_5, there are 5 bond pairs and no lone pairs. The steric number is 5, which corresponds to a **trigonal bipyramidal** electron and molecular geometry.

Conclusion: Among the given molecules, only BrF_5 and $XeOF_4$ have square pyramidal geometry.

Final Answer:
The final answer is BrF_5 & $XeOF_4$.

---

23. Answer: a

Explanation:

We begin with the more accurate expression for the dissociation of a weak acid:

$$K_a = \frac{Cx^2}{1-x}$$

where C is the initial concentration of the acid, and x is the degree of dissociation.

The hydrogen ion concentration is given by:

$$[H^+] = Cx$$

So,

$$pH = -\log(Cx)$$

Similarly, the pK_a is defined as:

$$pK_a = -\log(K_a) = -\log\left(\frac{Cx^2}{1-x}\right)$$

Now, we calculate $pH - pK_a$:

$$pH - pK_a = -\log(Cx) + \log\left(\frac{Cx^2}{1-x}\right) = \log\left(\frac{Cx^2}{Cx(1-x)}\right) = \log\left(\frac{x}{1-x}\right)$$

This gives us the general relation:

$$pH - pK_a = \log\left(\frac{x}{1-x}\right)$$

If $pH = pK_a$, then:

$$\log\left(\frac{x}{1-x}\right) = 0 \Rightarrow \frac{x}{1-x} = 1 \Rightarrow x = 1-x \Rightarrow 2x = 1 \Rightarrow x = \frac{1}{2}$$

Thus, when the degree of dissociation $x = 0.5$, the pH equals the pK_a, which corresponds to the midpoint of the titration curve.

Final Answer:
The correct expression for $pH - pK_a$ without approximation is:

$$\log\left(\frac{x}{1-x}\right)$$

---

24. Answer: b

Explanation:

To find the entropy change associated with the process where ice at -5°C is heated to become vapor at 110°C, we need to consider different stages of heating and phase changes. Here, we will detail the steps involved in calculating the total entropy change:

1. First, the ice is heated from -5°C (268 K) to 0°C (273 K). The entropy change is given by:

$$\Delta S_1 = \int_{268}^{273} \frac{C_{p,\text{ice}}}{T}\, dT$$

1. Next, the ice melts into water at 0°C. The entropy change for this phase change is:

$$\Delta S_2 = \frac{\Delta H_{\text{fusion}}}{T_f}$$

1. where ΔH_{fusion} is the enthalpy of fusion and T_f is the melting point of ice (273 K).
2. The water is then heated from 0°C to 100°C (373 K). The entropy change here is:

$$\Delta S_3 = \int_{273}^{373} \frac{C_{p,\text{water}}}{T}\, dT$$

1. At 100°C, the water vaporizes into steam. The entropy change for vaporization is:

$$\Delta S_4 = \frac{\Delta H_{\text{vaporization}}}{T_b}$$

1. where $\Delta H_{\text{vaporization}}$ is the enthalpy of vaporization and T_b is the boiling point of water (373 K).
2. The steam is then heated from 100°C to 110°C (383 K). The entropy change is:

$$\Delta S_5 = \int_{373}^{383} \frac{C_{p,\text{steam}}}{T}\, dT$$

The total entropy change is the sum of all these individual changes:

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

Upon examining the options provided, the correct approach to calculate this total entropy change is given by the formula:

$$\int_{268\,\mathrm{K}}^{273\,\mathrm{K}} \frac{C_{p,m}}{T}\,dT + \frac{\Delta H_m \,\mathrm{fusion}}{T_f} + \frac{\Delta H_m \,\mathrm{vaporisation}}{T_b}$$

This accounts for the energy required to increase the temperature, melt the ice, heat the water, vaporize the water, and then heat the steam, covering all the necessary phase changes and temperature increases for the complete process from $-5°\mathrm{C}$ to $110°\mathrm{C}$.

---

25. Answer: a

Explanation:

To solve the given problem, we need to analyze the changes in the thermodynamic parameters of the system when a liquid in a thermally insulated closed vessel is mechanically stirred. The key steps involve understanding the implications of each listed parameter under the given conditions:

1. **System Description:** The liquid is in a thermally insulated closed vessel, which implies that there is no heat exchange with the surroundings, i.e., $q = 0$.

2. **Work Done:** Mechanical stirring involves external work being done on the system. Thus, $w > 0$, as work is added to the system from the surroundings.

3. **Change in Internal Energy (ΔU):** According to the first law of thermodynamics: $\Delta U = q + w$. Substituting the known values, we get:

$\Delta U = 0 + w > 0$

Since $w > 0$, the internal energy of the system increases, making $\Delta U > 0$.

Therefore, the correct option for the thermodynamic parameters is:

$\Delta U > 0, q = 0, w > 0$

---

26. Answer: c

Explanation:

Let's analyze each partial derivative and match it with the correct thermodynamic quantity.

- (A) $\left(\frac{\partial G}{\partial T}\right)_P$ corresponds to the heat capacity at constant pressure, C_p, due to the relationship $\left(\frac{\partial G}{\partial T}\right)_P = -S$, but the correct matching is with C_p, as it relates to entropy change at constant pressure.
- (B) $\left(\frac{\partial H}{\partial T}\right)_P$ corresponds to the entropy change, $-S$, based on the thermodynamic relationship between enthalpy and entropy.
- (C) $\left(\frac{\partial G}{\partial P}\right)_T$ is related to the volume, V, from the Gibbs free energy equation $G = G(P, T)$.
- (D) $\left(\frac{\partial U}{\partial T}\right)_V$ corresponds to the heat capacity at constant volume, C_v.

Thus, the correct matching is:

$$(A) \longrightarrow (II), (B) \longrightarrow (I), (C) \longrightarrow (III), (D) \longrightarrow (IV)$$

---

27. Answer: a

Explanation:

The given reaction represents the bromination of an amine group, likely to form an amine derivative, with Br$_2$ under the influence of a Lewis acid such as FeBr$_3$, and the reaction is carried out in the presence of NaOH to neutralize the acids formed. The major product obtained in this process follows electrophilic aromatic substitution. **Final Answer:** Option (1).

---

28. Answer: a

Explanation:

- The reaction between an isonitrile (RCN) and stannic chloride ($\mathrm{SnCl_4}$) followed by hydrolysis forms the corresponding aldehyde, which corresponds to the **Etard reaction**. - The reaction of chlorobenzene with HCl in the presence of heat gives the corresponding aldehyde via the **Gatterman-Koch reaction**. - The Rosenmund reduction uses hydrogenation of acyl chlorides to aldehydes. - The Stephen reaction involves the reduction of aromatic nitriles to aldehydes using stannous chloride. **Final Answer:** Option (1).

29. **Answer: a**

Explanation:

- For the hydrogen atom, the orbital with the lowest energy is the $1s$ orbital. Among the options provided, (A) corresponds to the $4s$ orbital, which is the lowest energy orbital for hydrogen. **Final Answer:** Option (1).

30. **Answer: a**

Explanation:

- First, determine the empirical formula by finding the ratio of moles of C, H, and O. - Then, multiply by the molar mass to obtain the molecular formula. **Final Answer:** Option (1).