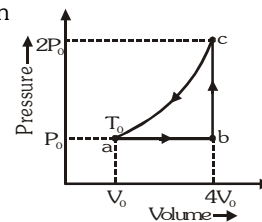


EXERCISE-01**CHECK YOUR GRASP****SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)**

1. The piece of zinc at a temperature of 20.0 C weighing 65.38 g is dropped into 180 g of boiling water ($T = 100\text{ C}$). The specific heat of zinc is $0.400\text{ J g}^{-1}\text{ C}^{-1}$ and that of water is $4.20\text{ J g}^{-1}\text{ C}^{-1}$. What is the final common temperature reached by both the zinc and water :-
(A) 97.3 C (B) 33.4 C (C) 80.1 C (D) 60.0 C
2. What is the change in internal energy ΔU , for a system that does 70 joules of work as it absorbs 45 joules of heat ?
(A) 115 J (B) 25 J (C) -25 J (D) -115 J
3. If the internal energy of an ideal gas decreases by the same amount as the work done by the system, the process is :-
(A) cyclic (B) isothermal (C) adiabatic (D) isolated
4. When 1 mol gas is heated at constant volume, temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct :-
(A) $q = W = 500\text{ J}$, $\Delta U = 0$ (B) $q = \Delta U = 500\text{ J}$, $W = 0$
(C) $q = W = 500\text{ J}$, $\Delta U = 0$ (D) $\Delta U = 0$, $q = W = -500\text{ J}$,
5. Internal energy does not include
(A) vibrational energy (B) rotational energy
(C) nuclear energy (D) energy arising by gravitational pull
6. Which one of the following quantity is dependent on path ?
(A) molar internal energy (B) volume (C) w (D) $q + w$
7. For a monatomic gas, the value of the ratio of $C_{p,m}$ and $C_{v,m}$ is :-
(A) $\frac{5}{3}$ (B) $\frac{7}{5}$ (C) $\frac{9}{7}$ (D) $\frac{9}{11}$
8. How much heat, in joules, must be added to 0.250 mol of Ar(g) to raise its temperature from 20 C to 36.0 C at constant pressure ?
(A) 50.0 (B) 83.2 (C) 187 (D) 200
9. In thermodynamics, a process is called reversible when :-
(A) surroundings and system change into each other
(B) there is no boundary between system and surroundings
(C) the surrounding are always in equilibrium with the system
(D) the system changes into the surroundings spontaneously
10. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then the change in the internal energy in expanding the gas from a to c along the path abc is :-
(A) $3P_0V_0$ (B) $6RT_0$
(C) $4.5RT_0$ (D) $10.5RT_0$
11. An adiabatic process is one in which there is no transfer of heat across the boundary between system and surroundings. For such a process.
(A) $P_{\text{ext}}\Delta V = 0$ (B) $q = w$ (C) $\Delta U = w$ (D) $\Delta U = 0$



12. Two moles of an ideal monoatomic gas are allowed to expand adiabatically and reversibly from 300 K and 200 K. The work done in the system is ($C_v = 12.5 \text{ J/K/mol}$)
- (A) -12.5 kJ (B) -2.5 kJ (C) -6.25 kJ (D) 500 kJ

13. One mole of an ideal monoatomic gas at temperature T and volume 1L expands to 2L against a constant external pressure of one atm under adiabatic conditions, then final temperature of gas will be :-

(A) $T + \frac{2}{3 \times 0.0821}$ (B) $T - \frac{2}{3 \times 0.0821}$ (C) $\frac{T}{2^{5/3-1}}$ (D) $\frac{T}{2^{5/3+1}}$

14. Enthalpy of the system is given as :-

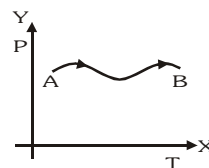
(A) $H + PV$ (B) $U + PV$ (C) $U - PV$ (D) $H - PV$

15. The P-T graph as given below was observed for a process of an ideal gas, which of the following statement is true :

(A) $w = +ve, \Delta H = +ve$ (B) $w = -ve, \Delta H = -ve$
 (C) $w = -ve, \Delta H = +ve$ (D) $w = +ve, \Delta H = -ve$

16. The difference between heats of reaction at constant pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25 in kJ mol^{-1} is :-

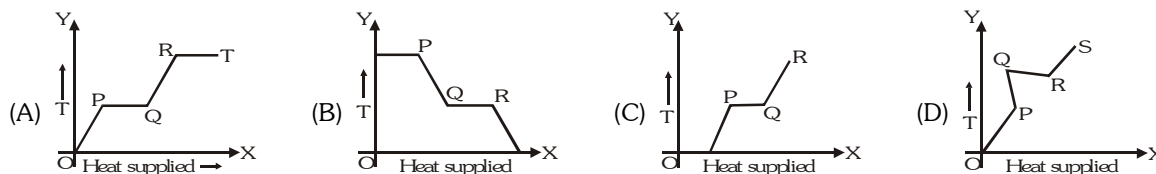
(A) -7.43 (B) +3.72
 (C) -3.72 (D) +7.43



17. The reaction $NH_2CN(s) + \frac{3}{2} O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$ was carried out at 300 K in a bomb calorimeter. The heat released was 743 kJ mol^{-1} . The value of ΔH_{300K} for this reaction would be :-

(A) $-740.5 \text{ kJ mol}^{-1}$ (B) $-741.75 \text{ kJ mol}^{-1}$ (C) $-743.0 \text{ kJ mol}^{-1}$ (D) $-744.25 \text{ kJ mol}^{-1}$

18. A block of ice at -10°C is slowly heated and converted into steam at 100°C . Which of the following curves represents the phenomenon qualitatively ?



19. How much energy must be supplied to change 36 g of ice at 0°C to water at room temperature 25°C

Data for water, H_2O $\Delta H_{\text{fusion}} = 6.01 \text{ kJ mol}^{-1}$ $C_{p,\text{liquid}} = 4.18 \text{ J.K}^{-1} \text{ g}^{-1}$

(A) 12 kJ (B) 16 kJ (C) 19 kJ (D) 22 kJ

20. Molar heat capacity of water in equilibrium with ice at constant pressure is :-

(A) zero (B) infinity
 (C) $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (D) $75.48 \text{ kJ K}^{-1} \text{ mol}^{-1}$

21. A vessel contains 100 litres of a liquid x. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy. The volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, $[U \rightarrow \text{total internal energy}]$:-

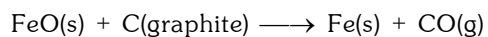
(A) $\Delta U = 0, \Delta H = 0$ (B) $\Delta U = +202.6 \text{ J}, \Delta H = +202.6 \text{ J}$
 (C) $\Delta U = -202.6 \text{ J}, \Delta H = -202.6 \text{ J}$ (D) $\Delta U = 0, \Delta H = +202.6 \text{ J}$

22. 1 mole of an ideal gas at 25 C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in J K⁻¹ mol⁻¹) :-
 (A) 19.15 (B) -19.15 (C) 4.7 (D) Zero
23. One mole of an ideal diatomic gas ($C_v = 5$ cal) was transformed from initial 25 C and 1 L to the state when temperature is 100 C and volume 10L. The entropy change of the process can be expressed as ($R = 2$ calories/mol/K) :-
 (A) $3 \ln \frac{298}{373} + 2 \ln 10$ (B) $5 \ln \frac{373}{298} + 2 \ln 10$
 (C) $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$ (D) $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$
24. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state, is $\Delta H = -401.7$ J mol⁻¹ for the transition. Assume the surrounding to be an ice-water both at 0 C :-
 (A) -1.09 JK⁻¹ (B) 1.47 JK⁻¹ (C) 0.38 JK⁻¹ (D) None of these
25. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is :-
 ($R = 0.082$ L atm mol⁻¹ K⁻¹ = 8.3 mol⁻¹ K⁻¹)
 (A) 0 (B) $R \ln(24.6)$ (C) $R \ln(2490)$ (D) $\frac{3}{2} R \ln(24.6)$
26. The enthalpy change for a given reaction at 298 K is $-x$ J mol⁻¹ (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature :
 (A) Can be negative but numerically larger than $\frac{x}{298}$
 (B) Can be negative but numerically smaller than $\frac{x}{298}$
 (C) Cannot be negative
 (D) Cannot be positive
27. For the gas - phase decomposition, $\text{PCl}_5(\text{g}) \xrightleftharpoons{\Delta} \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$:-
 (A) $\Delta H < 0, \Delta S < 0$ (B) $\Delta H > 0, \Delta S > 0$ (C) $\Delta H > 0, \Delta S < 0$ (D) $\Delta H < 0, \Delta S > 0$
28. A reaction has $\Delta H = -33$ kJ and $\Delta S = -58$ J/K. This reaction would be :-
 (A) Spontaneous at all temperature
 (B) Non-spontaneous at all temperature
 (C) Spontaneous above a certain temperature only
 (D) Spontaneous below a certain temperature only
29. If $\Delta G = -177$ K cal for (1) $2\text{Fe}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \longrightarrow \text{Fe}_2\text{O}_3(\text{s})$
 and $\Delta G = -19$ K cal for (2) $4\text{Fe}_2\text{O}_3(\text{s}) + \text{Fe}(\text{s}) \longrightarrow 3\text{Fe}_3\text{O}_4(\text{s})$
 What is the Gibbs free energy of formation of Fe_3O_4 ?
 (A) $+229.6 \frac{\text{kcal}}{\text{mol}}$ (B) $-242.3 \frac{\text{kcal}}{\text{mol}}$ (C) $-727 \frac{\text{kcal}}{\text{mol}}$ (D) $-229.6 \frac{\text{kcal}}{\text{mol}}$

30. Given the following data :

Substance	ΔH_f (kJ/mol)	S (J/mol K)
FeO(s)	-266.3	57.49
C(Graphite)	0	5.74
Fe(s)	0	27.28
CO(g)	-110.5	197.6

Determine at what temperature the following reaction is spontaneous ?

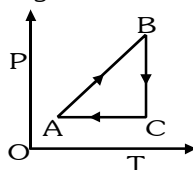


- (A) 298 K
 (B) 668 K
 (C) 966 K
 (D) ΔG is +ve, hence the reaction will never be spontaneous
-

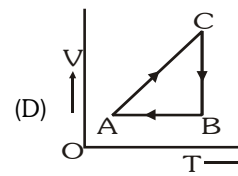
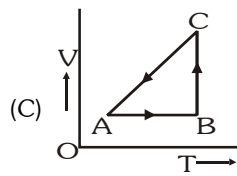
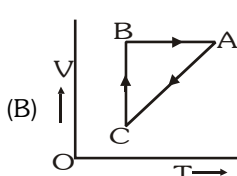
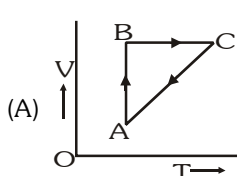
CHECK YOUR GRASP						ANSWER KEY				EXERCISE -1					
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	C	C	B	D	C	A	B	C	D	C	B	B	B	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	A	B	A	B	B	D	D	B	C	B	B	B	D	B	C

EXERCISE-02**BRAIN TEASERS****SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)**

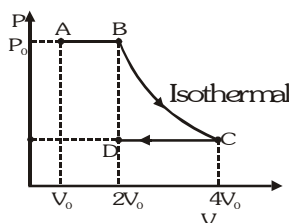
- Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV) Intensive properties are :
 (A) I, II (B) I, II, III (C) I, III, IV (D) all of these
- Which has maximum internal energy at 298 K ?
 (A) helium gas (B) oxygen gas (C) ozone gas (D) equal
- One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27 C. If the work done by the gas in the process is 3kJ, the final temperature will be equal to ($C_v = 20 \text{ J/K mol}$)
 (A) 100 K (B) 450 K (C) 150K (D) 400 K
- Two moles of an ideal gas ($C_v = \frac{5}{2} R$) was compressed adiabatically against constant pressure of 2 atm. which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to ?
 (A) 250 R (B) 300 R (C) 400 R (D) 500 R
- A cyclic process is shown in the P-T diagram.



Which of the curves show the same process on V-T diagram ?



- q , w , ΔE and ΔH for the following process ABCD on a monoatomic gas are :-



- (A) $w = -2P_0 V_0 \ln 2$, $q = 2P_0 V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$
 (B) $w = -2P_0 V_0 \ln 2$, $q = 2P_0 V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 2P_0 V_0 \ln 2$
 (C) $w = -P_0 V_0 (1 + \ln 2)$, $q = P_0 V_0 (1 + \ln 2)$, $\Delta E = 0$, $\Delta H = 0$
 (D) $w = -P_0 V_0 \ln 2$, $q = P_0 V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$
- One mole of a real gas is subjected to heating at constant volume from (P_1, V_1, T_1) state to (P_2, V_1, T_2) state. Then it is subjected to irrversible adiabatic compression against constant external pressure P_3 atm till system reaches final state (P_3, V_2, T_3). If the constant volume molar heat capacity of real gas is C_v . Find out correct expression for ΔH from state 1 to state 3.
- (A) $C_v (T_3 - T_1) + (P_3 V_1 - P_1 V_1)$ (B) $C_v (T_2 - T_1) + (P_3 V_2 - P_1 V_1)$
 (C) $C_v (T_2 - T_1) + (P_3 V_1 - P_1 V_1)$ (D) $C_p (T_2 - T_1) + (P_3 V_1 - P_1 V_1)$

8. The maximum efficiency of a heat engine operating between 100 C and 25 C is ?
 (A) 20% (B) 22.2% (C) 25% (D) None
9. A heat engine operating between 227 C and 27 C absorbs 2 kcal of heat from the 227 C reservoir reversibly per cycle. The amount of work done in one cycle is ?
 (A) 0.4 kcal (B) 0.8 kcal (C) 4 kcal (D) 8 kcal
10. A system is changed from an initial state to a final state by a manner such that $\Delta H = q$. If the same change from the initial state to the final state were made by a different path, which of the following statements are correct.
 (A) ΔH remain the same
 (B) ΔH will depend upon the type of path
 (C) Heat exchanged q will be same if the path is isobaric
 (D) Heat exchanged q will be different if the path is not isobaric
11. For which of the following reactions. ΔS will the maximum :-



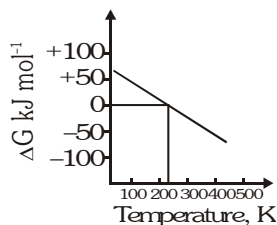
12. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300 C reversibly and isochorically ?

(A) $\frac{3}{2} R \ln \left(\frac{300}{200} \right)$ (B) $\frac{5}{2} R \ln \left(\frac{573}{273} \right)$ (C) $3R \ln \left(\frac{573}{473} \right)$ (D) $\frac{3}{2} R \ln \left(\frac{573}{473} \right)$

13. When two equal sized pieces of the same metal at different temperatures T_h (hot piece) and T_c (cold piece) are brought into contact into thermal contact and isolated from it's surrounding. The total change in entropy of system is given by ? [C_v (J/K) = heat capacity of metal]

(A) $C_v \ln \frac{T_c + T_h}{2T_c}$ (B) $C_v \ln \frac{T_2}{T_1}$ (C) $C_v \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$ (D) $C_v \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

14. What can be concluded about the values of ΔH and ΔS from this graph ?



- (A) $\Delta H > 0, \Delta S > 0$ (B) $\Delta H > 0, \Delta S < 0$ (C) $\Delta H < 0, \Delta S > 0$ (D) $\Delta H < 0, \Delta S < 0$
15. For which of the following processes, total entropy of universe increases.
 (A) Melting one mole of ice to water at 0 C
 (B) Freezing one mole of water to ice at 0 C
 (C) Freezing one mole of water to ice at - 10 C
 (D) Melting one mole of ice at 10 C into water
16. 9.0 g ice at 0 C is mixed with 36 g of water at 50 C in a thermally insulated container. Using the following data, answer the question that follow ?

$C_p (H_2O) = 4.18 J g^{-1} K^{-1}$; $\Delta H_{\text{fusion}} (\text{ice}) = 335 J g^{-1}$

- (i) final temperature of water is

(A) 304.43 K (B) 296.97 K (C) 303.93 K (D) 287 K

- (ii) ΔS_{ice} is
 (A) 11.04 JK^{-1} (B) 3.16 JK^{-1} (C) 14.2 JK^{-1} (D) 7.84 JK^{-1}
- (iii) ΔS_{water} is
 (A) -12.64 JK^{-1} (B) -0.34 JK^{-1} (C) -5.42 JK^{-1} (D) 12.64 JK^{-1}
- (iv) What is the total entropy change in the process ?
 (A) -1.56 JK^{-1} (B) -1.60 JK^{-1} (C) 1.56 JK^{-1} (D) 1.60 JK^{-1}
17. 1 mole of an ideal gas at 25 C is subjected to expand reversibly ten times of its initial volume. The change in entropy due to expansion is :-
 (A) $19.15 \text{ JK}^{-1} \text{ mole}^{-1}$ (B) $16.15 \text{ JK}^{-1} \text{ mole}^{-1}$
 (C) $22.15 \text{ JK}^{-1} \text{ mole}^{-1}$ (D) none
18. Following reaction occurs at 25 C :
 $2\text{NO} (\text{g}, 1 \times 10^{-5} \text{ atm}) + \text{Cl}_2 (\text{g}, 1 \times 10^{-2} \text{ atm}) \rightleftharpoons 2\text{NOCl} (\text{g}, 1 \times 10^{-2} \text{ atm}).$
 ΔG is :-
 (A) -45.65 kJ (B) -28.53 kJ (C) -22.82 kJ (D) -57.06 kJ
19. For the reaction at 300 K
 $\text{A}(\text{g}) + \text{B}(\text{g}) \longrightarrow \text{C}(\text{g})$
 $\Delta E = -3.0 \text{ kcal}$; $\Delta S = -10.0 \text{ cal/K}$ value of ΔG is ?
 (A) -600 cal (B) -6600 cal (C) -6000 cal (D) none
20. What is the free energy change (ΔG) when 1.0 mole of water at 100 C and 1 atm pressure is converted into steam at 100 C and 1 atm pressure ?
 (A) 80 cal (B) 540 cal (C) 620 cal (D) zero
21. What is the free energy change (ΔG) when 1.0 mole of water at 100 C and 1 atm pressure is converted into steam at 100 C and 2 atm pressure ?
 (A) zero cal (B) 540 cal (C) 515.4 cal (D) none

BRAIN TEASERS						ANSWER KEY				EXERCISE -2					
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	C	C	D	C	A	C	A	B	A,C	B	C	D	A	C,D
Que.	16 (i)	(ii)	(iii)	(iv)	17	18	19	20	21						
Ans.	B	C	A	C	A	A	A	D	C						

EXERCISE-03**MISCELLANEOUS TYPE QUESTIONS****TRUE / FALSE**

1. Pressure is an intensive property.
2. Like U and H, S is also a state function.
3. When a system undergoes a change at constant pressure, it is referred to an isothermal process.
4. The work done by a gas during free expansion is equal to zero.
5. First law of T.D. is applicable to all processes irrespective to whether they are reversible or irreversible.
6. All spontaneous process proceed in one direction only.
7. Positive value of ΔS_{system} during the process can be taken as sole criterion of spontaneity.
8. The ΔH of a reaction is independent of temperature.

FILL IN THE BLANKS

1. According to IUPAC conventions work done on the surroundings is
2. A system is said to be if it can neither exchange matter nor energy with surrounding.
3. The efficiency of a carnot engine can be increased by sink temperature when the source temperature is held constant.
4. Entropy change of a system is determine by the and states only, irrespective of how the system has changed its states.
5. Solidification of liquid shows in entropy.
6. When Fe(s) is dissolved in a aqueous HCl in a closed rigid vessel, the work done is
7. For Non-spontaneous process at constant T & P ΔG is

MATCH THE COLUMN

1.	Column-I (Process of reaction)	Column-II (Positive, negative)
(A)	For the process $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(s)}$, ΔH & ΔS are	(p) -ve, +ve
(B)	For the endothermic reaction $2\text{A}_{(s)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{A}_2\text{O}_{(s)}$ at 298 K, ΔS & ΔG are	(q) +ve, -ve
(C)	$\text{C(diamond)} \rightleftharpoons \text{C(graphite)}$, favourable conditions for formation of diamond are high pressure and high temperature then ΔH_f of diamond and ΔS_f of graphite from diamond are	(r) +ve, +ve
(D)	For the given reaction $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$, $E_{a(\text{forward})} = 57.2 \text{ kJ}$ and $E_{a(\text{backward})} = 3.2 \text{ kJ}$, ΔH & ΔS for the given reaction	(s) -ve, -ve

2.	Column-I (Process)	Column-II (Entropy change)
(A)	Reversible isothermal ideal gas expansion	(p) $\Delta S_{\text{surrounding}} = 0$
(B)	Reversible adiabatic ideal gas compression	(q) $\Delta S_{\text{surrounding}} < 0$
(C)	Adiabatic free expansion ($P_{\text{ext}} = 0$) of an ideal gas	(r) $\Delta S_{\text{surrounding}} > 0$
(D)	Irreversible isothermal ideal gas compression	(s) $\Delta S_{\text{system}} = 0$

ASSERTION & REASON

These questions contains, Statement I (assertion) and Statement II (reason).

- (A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.
 (B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for Statement-I
 (C) Statement-I is true, Statement-II is false.
 (D) Statement-I is false, Statement-II is true.

- Statement-I** : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Because

Statement-II : The volume occupied by the molecules of an ideal gas is zero.
- Statement-I** : The magnitude of the work involved in an isothermal expansion is greater than that involved in an adiabatic expansion.

Because

Statement-II : P-V curve (P on y-axis and V on x-axis) decrease more rapidly for reversible adiabatic expansion compared to reversible isothermal expansion starting from same initial state.
- Statement-I** : Entropy change in reversible adiabatic expansion of an ideal gas is zero.

Because

Statement-II : The increase in entropy due to volume increase just compensate the decrease in entropy due to fall in temperature.
- Statement-I** : The standard free energy changes of all spontaneously occurring reactions are negative.

Because

Statement-II : The standard free energies of the elements in their standard states at 1 bar and 298 K are taken as zero.
- Statement-I** : Enthalpy and entropy of any elementary substance in the standard states are taken as zero.

Because

Statement-II : At absolute zero, particles of the perfectly crystalline substance become completely ordered.
- Statement-I** : A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

Because

Statement-II : All exothermic reactions are accompanied by decrease of randomness.
- Statement-I** : Decrease of free energy during the process under constant temperature and pressure provides a measure of its spontaneity.

Because

Statement-II : A spontaneous change must have +ve sign of ΔS_{system} .

COMPREHENSION BASED QUESTIONS

Comprehension # 1

An ideal gas, having ratio of specific heat γ undergoes a process in which its internal energy relates to the volume as $U = \alpha\sqrt{V}$, where α is a constant. If the gas is expanded from volume V_1 to V_2 .

1. The work performed by gas is :

(A) $2\alpha(\gamma - 1)[\sqrt{V_2} - \sqrt{V_1}]$

(B) $\alpha(\gamma - 1)[\sqrt{V_2} - \sqrt{V_1}]$

(C) $2\alpha(\gamma - 1)[V_2 - V_1]$

(D) $\alpha(\gamma - 1)[V_2 - V_1]$

2. If the ideal gas is diatomic and its increase in internal energy is 100 J then the work performed by gas is : (Ignore vibrational degree of freedom)

(A) 80 J

(B) 180 J

(C) 100 J

(D) 20 J

3. In the above question, the heat supplied to gas is :

(A) 80 J

(B) 180 J

(C) 100 J

(D) 20 J

Comprehension # 2

Standard Gibb's energy of reaction ($\Delta_r G$) at a certain temperature can be computed as $\Delta_r G = \Delta_r H - T \Delta_r S$ and the change in the value of $\Delta_r H$ and $\Delta_r S$ for a reaction with temperature can be computed as follows :

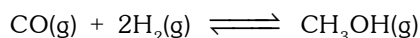
$$\Delta_r H_{T_2}^\circ - \Delta_r H_{T_1}^\circ = \Delta_r C_p^\circ (T_2 - T_1)$$

$$\Delta_r S_{T_2}^\circ - \Delta_r S_{T_1}^\circ = \Delta_r C_p^\circ \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

and by $\Delta_r G = -RT \ln K_{eq}$

Consider the following reaction :



Given : $\Delta_f H$ ($\text{CH}_3\text{OH, g}$) = -201 kJ/mol ; $\Delta_f H$ (CO, g) = - 114 kJ/mol

S ($\text{CH}_3\text{OH, g}$) = 240 J/K-mol ;

S (H_2, g) = 29 JK⁻¹ mol⁻¹

S (CO, g) = 198 J/mol-K ;

$C_{p, m}$ (H_2) = 28.8 J/mol-K

$C_{p, m}$ (CO) = 29.4 J/mol-K ;

$C_{p, m}$ (CH_3OH) = 44 J/mol-K

and $\ln\left(\frac{320}{300}\right) = 0.06$, all data at 300 K

1. $\Delta_r S$ at 300 K for the reaction is :

(A) 152.6 J/K-mol

(B) 181.6 J/K-mol

(C) -16 J/K-mol

(D) none of these

2. $\Delta_r H$ at 300 K for the reaction is :

(A) -87 kJ/mol

(B) 87 kJ/mol

(C) -315 kJ/mol

(D) -288 kJ/mol

3. $\Delta_r S$ at 320 K is :

(A) 155.18 J/mol-K

(B) 150.02 J/mol-K

(C) 172 J/mol-K

(D) none of these

4. $\Delta_f H$ at 320 K is :
 (A) -288.86 kJ/mol (B) -289.1 kJ/mol
 (C) -87.86 kJ/mol (D) none of these
5. $\Delta_f G$ at 320 K is :
 (A) -48295.2 kJ/mol (B) -240.85 kJ/mol
 (C) 240.85 kJ/mol (D) -81.91 kJ/mol
-

MISCELLANEOUS TYPE QUESTION	ANSWER KEY	EXERCISE -3
<ul style="list-style-type: none"> <u>True / False</u> <ol style="list-style-type: none"> 1. T 2. T 3. F 4. T 5. T 6. T 7. F 8. F <u>Fill in the Blanks</u> <ol style="list-style-type: none"> 1. Negative 2. isolated 3. decreasing 4. (i) initial (ii) final 5. decrease 6. zero 7. positive <u>Match the Column</u> <ol style="list-style-type: none"> 1. (A) \rightarrow s ; (B) \rightarrow p ; (C) \rightarrow r ; (D) \rightarrow r 2. (A) \rightarrow q ; (B) \rightarrow p,s ; (C) \rightarrow p ; (D) \rightarrow r <u>Assertion - Reason Questions</u> <ol style="list-style-type: none"> 1. B 2. A 3. A 4. B 5. D 6. C 7. C <u>Comprehension Based Questions</u> <ol style="list-style-type: none"> Comprehension #1 : 1. (A) 2. (A) 3. (B) Comprehension #2 : 1. (C) 2. (A) 3. (D) 4. (C) 5. (D) 		

EXERCISE-04 [A]**CONCEPTUAL SUBJECTIVE EXERCISE**

1. In which of the following changes at constant pressure is work done by system on surrounding ? By the surrounding on system ?

Initial state		Final state
(i) $\text{H}_2\text{O} (\text{g})$	\longrightarrow	$\text{H}_2\text{O}(\ell)$
(ii) $\text{H}_2\text{O} (\text{s})$	\longrightarrow	$\text{H}_2\text{O}(\text{g})$
(iii) $\text{H}_2\text{O} (\ell)$	\longrightarrow	$\text{H}_2\text{O}(\text{s})$
(iv) $3\text{H}_2 (\text{g}) + \text{N}_2(\text{g})$	\longrightarrow	$2\text{NH}_3(\text{g})$
(v) $\text{CaCO}_3 (\text{s})$	\longrightarrow	$\text{CaO} (\text{s}) + \text{CO}_2(\text{g})$

2. The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J which is exchanged with the surroundings. What are q, w and ΔE ?
3. The enthalpy of combustion of glucose is $-2808 \text{ kJ mol}^{-1}$ at 25 C. How many grams of glucose do you need to consume [Assume wt = 62.5 Kg].
- (a) To climb a flight of stairs rising through 3m.
- (b) To climb a mountain of altitude 3000 m ?

Assume that 25% of enthalpy can be converted to useful work.

4. What is ΔE when 2.0 mole of liquid water vaporises at 100 C ? The heat of vaporisation, ($\Delta H_{\text{vap.}}$) of water at 100 C is $40.66 \text{ kJ mol}^{-1}$.
5. If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the process.
6. When the following reaction was carried out in a bomb calorimeter, ΔE is found to be -742.7 kJ/mol of $\text{NH}_2\text{CN} (\text{s})$ at 298 K.
- $$\text{NH}_2\text{CN}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$$
- Calculate ΔH_{298} for the reaction.
7. When 1 mole of ice melt at 0 C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔE for the reaction.
8. Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.
9. One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27 C in a cylinder fitted with a piston. Find the value of ΔE , q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.



10. Five moles of an ideal gas at 300K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext. pressure of 1 atm. Calculate q, w, ΔU & ΔH . Calculate the corresponding value of all if the above process is carried out reversibly.
11. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

(a) What is final temperature

(b) What is work done.

Given $\gamma = 1.33$ and $C_V = 25.08 \text{ J mol}^{-1} \text{ K}^{-1}$ for CO_2 .

12. A sample of a fluorocarbon was allowed to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 to 248.44 K. Assume the gas behaves perfectly. Estimate the value of $C_{V, m}$.

13. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25 C ?

14. One mole of an ideal monoatomic gas is carried through the cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

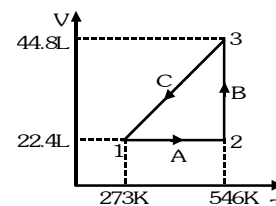


Table-1			
State	P	V	T
1			
2			
3			

Step	Name of process	q	w	ΔE	ΔH
A					
B					
C					
overall					

15. The standard enthalpy of formation of water liquid is -285.76 kJ at 298 K. Calculate the value at 373K. The molar heat capacities at constant pressure (C_p) in the given temperature range of $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are respectively 38.83, 29.16 and $75.312 \text{ JK}^{-1} \text{ mol}^{-1}$.

16. Methane (Considered to be an ideal gas) initially at 25 C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by :

$C_p = 22.34 + 48.1 \times 10^{-3} T$. where C_p is in $\text{JK}^{-1} \text{ mol}^{-1}$. Calculate molar (a) ΔH (b) ΔU .

17. One mole of $\text{NaCl}(\text{s})$ on melting absorbed 30.5 kJ of heat and its entropy is increased by 28.8 JK^{-1} . What is the melting point of sodium chloride ?

18. Oxygen is heated from 300 K to 600 K at a constant pressure of 1 bar. What is the increases in molar entropy? The molar heat capacity in $\text{JK}^{-1} \text{ mol}^{-1}$ for the O_2 is.

$$C_p = 25.5 + 13.6 \times 10^{-3} T - 42.5 \times 10^{-7} T^2$$

19. Calculate the free energy change at 298 K for the reaction :

$\text{Br}_2(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{BrCl}(\text{g})$. For the reaction $\Delta H = 29.3 \text{ kJ}$ & the entropies of $\text{Br}_2(\text{l})$, $\text{Cl}_2(\text{g})$ & $\text{BrCl}(\text{g})$ at the 298 K are 152.3, 223.0, $239.7 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively.

20. Using the data given below, establish that the vaporization of $\text{CCl}_4(l)$ at 298K to produce $\text{CCl}_4(g)$ at 1 atm pressure does not occur spontaneously.

Given : $\text{CCl}_4(l, 1 \text{ atm}) \longrightarrow \text{CCl}_4(g, 1 \text{ atm})$; $\Delta S = 94.98 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\Delta H_f(\text{CCl}_4, g) = -106.7 \text{ kJ mol}^{-1} \text{ \& } \Delta H_f(\text{CCl}_4, l) = -139.3 \text{ kJ mol}^{-1}$$

21. From the given table answer the following questions :

Reaction : $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$

- (i) Calculate $\Delta_r H_{298}$ (ii) Calculate $\Delta_r G_{298}$
 (iii) Calculate $\Delta_r S_{298}$ (iv) Calculate $\Delta_r E_{298}$
 (v) Calculate $S_{298}[\text{H}_2\text{O}(g)]$

	$\text{CO}(g)$	$\text{CO}_2(g)$	$\text{H}_2\text{O}(g)$	$\text{H}_2(g)$
$\Delta H_{298} \text{ (-kJ/mol)}$	-26.42	-94.05	-57.8	0
$\Delta G_{298} \text{ (-kJ/mol)}$	-32.79	-94.24	-54.64	0
$S_{298} \text{ (-Cal/kmole)}$	47.3	51.1	?	31.2

CONCEPTUAL SUBJECTIVE EXERCISE	ANSWER KEY	EXERCISE-4(A)
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1. (i) + w, (ii) - w, (iii) + w, (iv) + w, (v) - w 2. $q = -65 \text{ J}$, $w = 20 \text{ J}$, $\Delta E = -45 \text{ J}$
 3. (A) 0.47 g, (B) 0.47 kg 4. $\Delta E = 75.11 \text{ kJ}$
 5. $\Delta E = 0.993 \text{ kcal}$, $\Delta H = 1 \text{ kcal}$ 6. -741.5 kJ
 7. $\Delta H \cong \Delta E = 1440 \text{ calories}$ 8. -10 J
 9. $\Delta E = -39.03 \text{ kJ mol}^{-1}$, $q = -36.5 \text{ kJ}$, $w = -2.53 \text{ J}$
 10. $w_{\text{irr}} = -9356.25 \text{ J}$, $w_{\text{rev}} = -17291.6 \text{ J}$, $\Delta U = \Delta H = 0$
 11. $T_2 = 100 \text{ K}$, $w = -5.016 \text{ kJ}$
 12. $C_{v,m} = 31.6 \text{ J K}^{-1} \text{ mol}^{-1}$ 13. $w = -3.988 \text{ kJ}$

14.

State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	$3/2 R(273)$	0	$3/2 R(273)$	$5/2 R(273)$
B	Isothermal	$546 R \ln 2$	$-546 R \ln 2$	0	0
C	Isobaric	$-5/2 R(273)$	$R(273)$	$-3/2 R(273)$	$-5/2 R(273)$
overall	cyclic	$546 R \ln 2 - 273 R$	$273 R - 546 R \ln 2$	0	0

15. $\Delta H_{373}^\circ(\text{H}_2\text{O}, (l)) = -284.11 \text{ kJ}$ 16. (a) $13.064 \text{ kJ mol}^{-1}$ (b) $10.587 \text{ kJ mol}^{-1}$
 17. $T = 1059 \text{ K}$ 18. $21.18 \text{ J K}^{-1} \text{ mol}^{-1}$
 19. -1721.8 J 20. $\Delta G = 4.3 \text{ kJ mol}^{-1} > 0$
 21. (i) $-9.83 \text{ kcal mol}^{-1}$ (ii) $-6.81 \text{ kcal mol}^{-1}$
 (iii) -10.13 cal/K mol (iv) -9.83 kcal/mol
 (v) $+45.13 \text{ cal/K mole}$

EXERCISE-04 [B]

BRAIN STORMING SUBJECTIVE EXERCISE

1. The increase in entropy of 1 kg of ice at 200 K which is heated to 400 K (super heated steam) at constant atmospheric pressure, will be :
Given that $C_p(\text{ice}) = 2.09 \times 10^3 \text{ J/kg degree}$; $C_p(\text{water}) = 4.18 \times 10^3 \text{ J/kg degree}$
 $C_p(\text{steam}) = 2.09 \times 10^3 \text{ J/kg degree}$; $L_f(\text{C}, 273 \text{ K}) = 3.34 \times 10^5 \text{ J/kg}$;
 $L_v(\text{water}, 273 \text{ K}) = 22.6 \times 10^5 \text{ J/kg}$
2. Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1 atm to final pressure of 2 atm. Initial temperature = 300 K
 - (a) If process is carried out reversibly.
 - (b) If process is carried out irreversible against 2 atm external pressure.Compute the final volume reached by gas in two cases.
3. 20.0 dm^3 of an ideal gas (diatomic $C_{v,m} = 5 \text{ R}/2$) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q , w , ΔU and ΔH for the process if the expansion is :
 - (i) Isothermal and reversible
 - (ii) Adiabatic and reversible
 - (iii) Isothermal and adiabatic
 - (iv) Against 0.2 MPa and adiabatic
 - (v) Against 0.2 MPa and isothermal.
4. One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of ΔS_{gas} and ΔS_{total} under the following conditions.
 - (i) Expansion is carried out reversibly.
 - (ii) Expansion is carried out irreversibly where 836.6 J of heat is less absorbed than in (i)
 - (iii) Expansion is free.
5. 10 g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.
 - (i) Expansion is carried out reversibly.
 - (ii) Expansion occurs against a constant external pressure of 202.65 kPa.
 - (iii) Expansion is free expansion.
6. Pressure over 1000 mL of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure.
7. One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate ΔS_{system} , ΔS_{surr} , and ΔS_{total} in
 - (i) when the process carried out reversibly
 - (ii) when the process carried out irreversibly (one step)
8. Fixed amount of an ideal gas contained in a sealed rigid vessel ($V = 24.6 \text{ litre}$) at 1.0 bar is heated reversibly from 27 C to 127 C. Determine change in Gibb's energy (in Joule) if entropy of gas $S = 10 + 10^{-2} T \text{ (J/K)}$.
9. A 32 g sample of CH_4 gas initially at 101.325 kPa and 300 K is heated to 550 K. $C_{p,m}/\text{JK}^{-1} \text{ mol}^{-1} = 12.552 + 8.368 \times 10^{-2} T/\text{K}$. Assuming CH_4 behaves ideally, compute w , q , ΔU and ΔH for (a) an isobaric reversible process and (b) an isochoric reversible process.
10. At 298 K, $\Delta H_{\text{combustion}}(\text{sucrose}) = -5737 \text{ kJ/mol}$ & $\Delta G_{\text{combustion}}(\text{sucrose}) = -6333 \text{ kJ/mol}$. Estimate additional non-PV work that is obtained by raising temperature to 310 K. Assume $\Delta_f C_p = 0$ for this temperature change.

11. Compute $\Delta_r G$ for the reaction $\text{H}_2\text{O}(\ell, 1 \text{ atm}, 323 \text{ K}) \rightarrow \text{H}_2\text{O}(\text{g}, 1 \text{ atm}, 323 \text{ K})$
 Given that : $\Delta_{\text{vap}} H$ at $373 \text{ K} = 40.639 \text{ kJ mol}^{-1}$, $C_p(\text{H}_2\text{O}, \ell) = 75.312 \text{ J K}^{-1} \text{ mol}^{-1}$,
 $C_p(\text{H}_2\text{O}, \text{g}) = 33.305 \text{ J K}^{-1} \text{ mol}^{-1}$.
12. (a) An ideal gas undergoes a single state expansion against a constant opposing pressure from (P_1, V_1, T) to (P_2, V_2, T) . What is the largest mass m which can be lifted through a height h in this expansion ?
 (b) The system (a) restored to its initial state by a single state compression. What is the smallest mass m' which must fall through the height h to restore system?
 (c) What is the net mass lowered through height h in the cyclic transformation in (a) and (b) ?

BRAIN STORMING SUBJECTIVE EXERCISE	ANSWER KEY	EXERCISE-4(B)
1.	9390 J kg^{-1}	
2.	(a) $T_2 = 395.8$; $V_2 = 16.24 \text{ L}$; $w_{\text{rev}} = 1194.72 \text{ J}$, (b) $V_2^1 = 17.24 \text{ L}$; $T_2^1 = 420 \text{ K}$; $w_{\text{irrev}} = 1496.52 \text{ J}$	
3.	(i) $q = -w = 17.54 \text{ kJ}$, $\Delta U = 0$ and $\Delta H = 0$; (ii) $q = 0$, $w = \Delta U = -10.536 \text{ kJ}$ and $\Delta H = -14.75 \text{ kJ}$ (iii) $q = 0$, $w = 0$, $\Delta U = 0$ and $\Delta H = 0$; (iv) $q = 0$; $\Delta U = w = -7.14 \text{ kJ}$; $\Delta H = -9.996 \text{ kJ}$ (v) $q = -w = 9.94 \text{ kJ}$, $\Delta U = \Delta H = 0$	
4.	$\Delta S_{\text{gas}} = -\Delta S_{\text{surr}}$ and $\Delta S_{\text{total}} = 0$, (ii) $\Delta S_{\text{total}} = 2.808 \text{ J K}^{-1}$, (iii) $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 9.134 \text{ J K}^{-1}$	
5.	(i) $\Delta S_{\text{sys}} = 0$; $\Delta S_{\text{surr}} = 0$ and $\Delta S_{\text{total}} = 0$, (ii) $\Delta S_{\text{surr}} = 0$; $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 0.957 \text{ JK}^{-1}$ (iii) $\Delta S_{\text{sys}} = \Delta S_{\text{total}} = 3.81 \text{ JK}^{-1}$	
6.	$\Delta U = 501 \text{ J}$; $\Delta H = 99.5 \text{ kJ}$	
7.	(i) Rev. process $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$; $\Delta S_{\text{surr}} = -\frac{3}{2} R \ln 10$, (ii) Irr. process $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$; $\Delta S_{\text{surr}} = -\frac{3}{2} (0.9)$; $\Delta S_{\text{total}} = \frac{3}{2} R (1.403)$	
8.	-530 J	
9.	(a) $q_p = \Delta H = 24.058 \text{ kJ}$, $w = -4.157 \text{ kJ}$, $\Delta U = 19.90 \text{ kJ}$; (b) $\Delta U = 19.90 \text{ kJ}$, $\Delta H = 24.058$; $w = 0$	
10.	24 kJ/mol	11. $\Delta_r G = 5.59 \text{ kJ mol}^{-1}$
12.	(a) $m = m = \frac{nRT}{gh} \left(1 - \frac{P_2}{P_1} \right)$, (b) $m' = \frac{nRT}{gh} \left(\frac{P_1}{P_2} - 1 \right)$, (c) $m' - m = \frac{nRT}{gh} \left(\frac{(P_1 - P_2)^2}{P_1 P_2} \right)$	

EXERCISE-05(A)**PREVIOUS YEARS QUESTIONS**

1. In a irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (ΔG) and change in entropy (ΔS) satisfy the criteria :-
[AIEEE-2003]
(1) $(\Delta S) = 0, (\Delta G) = 0$
(2) $(\Delta S) = 0, (\Delta G) > 0$
(3) $(\Delta S) < 0, (\Delta G) < 0$
(4) $(\Delta S) > 0, (\Delta G) < 0$
2. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ?
[AIEEE-2003]
(1) < 40 kJ
(2) Zero
(3) 40 kJ
(4) > 40 kJ
3. The enthalpy change for a reaction does not depend upon :-
[AIEEE-2003]
(1) The nature of intermediate reaction steps
(2) The differences in initial or final temperatures of involved substances
(3) The physical states of reactants and products
(4) Use of different reactants for the same product
4. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is :-
[AIEEE-2003]
(1) $\Delta G = RT \ln K_c$
(2) $-\Delta G = RT \ln K_c$
(3) $\Delta G = RT \ln K_c$
(4) $-\Delta G = RT \ln K_c$
5. In conversion of lime-stone to lime,
 $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
the values of ΔH and ΔS are $+179.1 \text{ kJ mol}^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH and ΔS do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-
[AIEEE-2007]
(1) 1008 K
(2) 1200 K
(3) 845 K
(4) 1118 K
6. Identify the correct statement regarding a spontaneous process :-
[AIEEE-2007]
(1) For a spontaneous process in an isolated system, the change in entropy is positive
(2) Endothermic processes are never spontaneous
(3) Exothermic processes are always spontaneous
(4) Lowering of energy in the reaction process is the only criterion for spontaneity
7. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively. For the reaction,
 $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$, $\Delta H = -30 \text{ kJ}$, to be at equilibrium, the temperature will be
[AIEEE-2008]
(1) 1250 K
(2) 500 K
(3) 750 K
(4) 1000 K

8. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm³ to a volume of 100 dm³ at 27 C is :- [AIEEE-2011]
- (1) 32.3 J mol⁻¹ K⁻¹ (2) 42.3 J mol⁻¹ K⁻¹
 (3) 38.3 J mol⁻¹ K⁻¹ (4) 35.8 J mol⁻¹ K⁻¹
9. The incorrect expression among the following is :- [AIEEE-2012]
- (1) $K = e^{-\Delta G / RT}$
 (2) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = - T$
 (3) In isothermal process, $W_{\text{reversible}} = - nRT \ln \frac{V_f}{V_i}$
 (4) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$
10. One mole of an ideal gas is expanded isothermally and reversibly to half its initial pressure. ΔS for the process in J K⁻¹ mol⁻¹ is [ln 2 = 0.693 and R = 8.314, J/(mol/K)] : [AIEEE-2012 (Online)]
- (1) 10.76 (2) 6.76 (3) 8.03 (4) 5.76
11. The entropy of a sample of a certain substance increases by 0.836 JK⁻¹ on adding reversibly 0.3344 J of heat at constant temperature. The temperature of the sample is :- [AIEEE-2012 (Online)]
- (1) 0.4 K (2) 2.5 K (3) 0.016 K (4) 0.3 K
12. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0 C. As it does so, it absorbs 208J of heat. The values of q and w for the process will be :- [JEE(Main)-2013]
- (R = 8.314 J/mol K) (ln 7.5 = 2.01)
- (1) q = + 208 J, w = - 208 J (2) q = - 208 J, w = - 208 J
 (3) q = - 208 J, w = + 208 J (4) q = + 208 J, w = + 208 J

PREVIOUS YEAR QUESTIONS ANSWER KEY EXERCISE-5(A)													
Que.	1	2	3	4	5	6	7	8	9	10	11	12	
Ans	4	2	1	2	4	1	3	3	4	4	2	1	

EXERCISE-05(B)**PREVIOUS YEARS QUESTIONS**

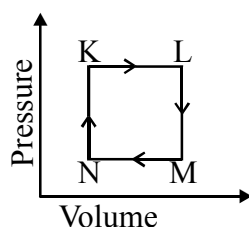
1. A process $A \longrightarrow B$ is difficult to occur directly instead it takes place in three successive steps :-
- $\begin{array}{c} C \longrightarrow D \\ \uparrow \qquad \downarrow \\ A \qquad B \end{array}$

$\Delta S(A \longrightarrow C) = 50 \text{ e.u.}$
 $\Delta S(C \longrightarrow D) = 30 \text{ e.u.}$
 $\Delta S(B \longrightarrow D) = 20 \text{ e.u.}$
- where e.u. is entropy unit.
- Then the entropy change ΔS for the process $(A \longrightarrow B)$ is [IIT-JEE-2006]
- (A) +100 e.u. (B) -60 e.u. (C) -100 e.u. (D) +60 e.u.
2. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one :- [IIT-JEE-2006]
- (A) $4/2 R$ (B) $3/2 R$ (C) $5/2 R$ (D) zero
3. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temp. ($R = 0.0821 \text{ litre. atm K}^{-1} \text{ mol}^{-1}$) [IIT-JEE-2005]
- (A) T (B) $\frac{T}{(2)^{\frac{5}{3}-1}}$ (C) $T - \frac{2}{3 \times 0.0821}$ (D) $T + \frac{2}{3 \times 0.0821}$
4. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is :- [IIT-JEE-2004]
- (A) 11.4 kJ (B) -11.4 kJ (C) 0 kJ (D) 4.8 kJ
5. The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is $75 \text{ J mol}^{-1} \text{ K}$. The boiling point of the liquid at 1 atm is :- [IIT-JEE-2004]
- (A) 250 K (B) 400 K (C) 450 K (D) 600 K
6. One mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm :- [IIT-JEE-2002]
- (A) 40.0
(B) 42.3
(C) 44.0
(D) not defined, because pressure is not constant
7. Which of the following statement is false ? [IIT-JEE-2001]
- (A) Work is a state function
(B) temperature is a state function
(C) Change of state is completely defined when initial and final states are specified
(D) Work appears at the boundary of the system
8. Molar heat capacity of water in equilibrium with ice at constant pressure is :- [IIT-JEE-1997]
- (A) zero (B) ∞
(C) $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (D) $75.48 \text{ JK}^{-1} \text{ mol}^{-1}$
9. For the reaction, [IIT-JEE-2006]
- $$2\text{CO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)} ; \Delta H = -560 \text{ kJ mol}^{-1}$$
- In one litre vessel at 500 K the initial pressure is 70 atm and after the reaction it becomes 40 atm at constant volume of one litre. Calculate change in internal energy. All the above gases show significant deviation from ideal behaviour. (1 Latm = 0.1 kJ)

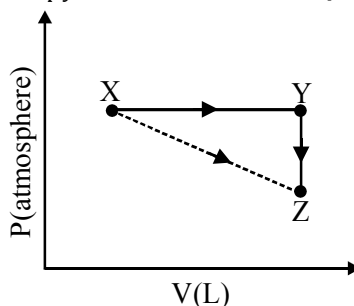
10. One mole of a liquid (1 bar, 100 mL) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decreases by 1 mL. Find ΔU and ΔH [IIT-JEE-2004]
11. Two moles of a perfect gas undergoes the following processes : [IIT-JEE-2002]
- a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L) ;
 - a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L) ;
 - a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L) ;
- Sketch with labels each of the processes on the same P-V diagram.
 - Calculate the total work (w) and the total heat change (q) involved in the above processes.
 - What will be the values of ΔU , ΔH and ΔS for the overall process ?
12. Show that the reaction $\text{CO(g)} + \frac{1}{2} \text{O}_2 \text{(g)} \longrightarrow \text{CO}_2 \text{(g)}$ at 300 K is spontaneous and exothermic, when the standard entropy is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively. [IIT-JEE-2001]
13. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3 . Calculate the enthalpy change in this process. $C_{v,m}$ for argon is $12.48 \text{ JK}^{-1} \text{ mol}^{-1}$. [IIT-JEE-2000]

Paragraph for Question 14 and 15

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. [JEE 2013]



14. The pair of isochoric processes among the transformation of states is
- K to L and L to M
 - L to M and N to K
 - L to M and M to N
 - M to N and N to K
15. The succeeding operations that enable this transformation of states are
- Heating, cooling, heating, cooling
 - cooling, heating, cooling, heating
 - Heating, cooling, cooling, heating
 - Cooling, heating, heating, cooling
16. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct ? [take ΔS as change in entropy and w as work done] [JEE 2012]



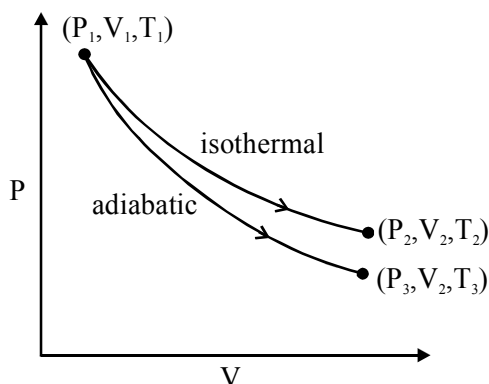
(A) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$

(B) $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$

(C) $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$

(D) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

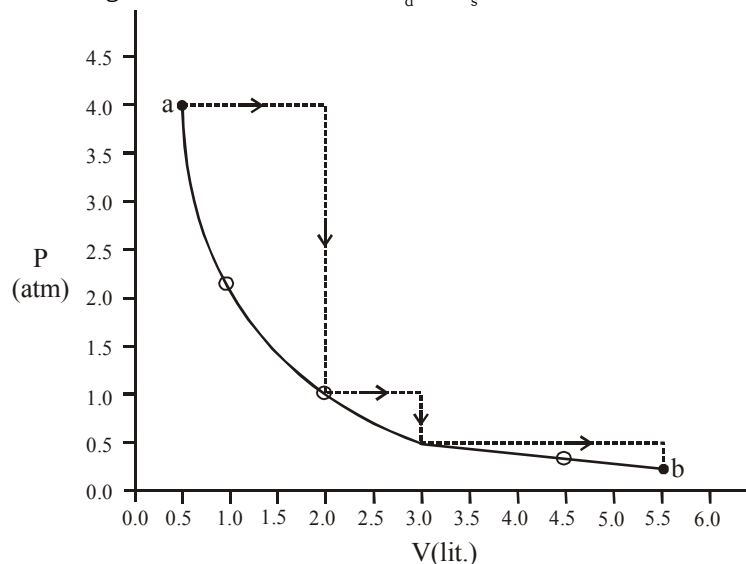
17. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? [JEE 2012]



- (A) $T_1 = T_2$ (B) $T_3 > T_1$ (C) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ (D) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$
18. Match the transformations in **Column-I** with appropriate option in **Column-II** [JEE 2011]

Column-I	Column-II
(A) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$	(p) phase transition
(B) $\text{CaCO}_3(\text{g}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(q) allotropic change
(C) $2\text{H}\cdot \rightarrow \text{H}_2(\text{g})$	(r) ΔH is positive
(D) $\text{P}_{(\text{white, solid})} \rightarrow \text{P}_{(\text{red, solid})}$	(s) ΔS is positive
	(t) ΔS is negative

19. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , then the integer closed to the ratio w_d / w_s is- [JEE 2010]



20. Among the following, the state function(s) is (are) [JEE 2009]
 (A) Internal energy (B) Irreversible expansion work
 (C) Reversible expansion (D) Molar enthalpy
21. **Statement-1** : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. [JEE 2008]
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
22. **Statement-1** : There is a natural asymmetry between converting work to heat and converting heat to work.
Statement-2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. [JEE 2008]
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.
23. For the process $\text{H}_2\text{O}(\text{l})$ (1 bar, 373 K) \longrightarrow $\text{H}_2\text{O}(\text{g})$ (1 bar, 373 K), the correct set of thermodynamic parameters is :- [JEE 2007]
 (A) $\Delta G = 0$, $\Delta S = +ve$ (B) $\Delta G = 0$, $\Delta S = -ve$
 (C) $\Delta G = +ve$, $\Delta S = 0$ (D) $\Delta G = -ve$, $\Delta S = +ve$

PREVIOUS YEARS QUESTIONS				ANSWER KEY		EXERCISE -5(B)
1. (D)	2. (A)	3. (C)	4. (C)			
5. (B)	6. (C)	7. (A)	8. (B)			
9. -557 kJ/mol						
10. $\Delta U = 0.1$ litre atm, $\Delta H = 9.9$ litre atm						
11. (ii) $-w = q = 620.77$ J, (iii) $\Delta H = 0$, $\Delta U = 0$, $\Delta S = 0$						
12. $\Delta H = -285.4$ kJ/mol, $\Delta G = -257.2$ kJ/mol	0					
13. $\Delta H = -114.52$ J						
14. (B)	15. (C)	16. (A), (C)	17. (A), (D)			
18. (A) \rightarrow (p, r, s) ; (B) \rightarrow (r, s) ; (C) \rightarrow (t) ; (D) \rightarrow (p, q, t)						
19. (2)	20. (A), (D)	21. (D)	22. (A)			
23. (A)						