THERMODYNAMICS IInd & IIIrd LAW

Exercise-1

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Introduction about entropy

A-1. The entropy of a gas increases on its expansion. Why ?

A-2. Entropy of the solutions is higher than that of pure liquid. Why ?

A-3.✍ What are the signs of ΔS for the system and for the surrounding in each of the following processes ?
(a) Water boils in a teakettle on a hot stove.
(b) Ice in an ice cube tray, left an a table melts.
(c) A cup of coffee is reheated in a microwave oven.

A-4. State the second law of thermodynamics.

A-5. Write statement of IIIrd law of thermodynamics ?

A-6. State the thermodynamic condition of spontaneous occurance of a process ?

A-7. If ΔH for a reaction has a positive value, how would you know the sign requirement of ΔS for it so that the reaction is spontaneous ?

Section (B) : Entropy Calculation

B-1. The entropy of vaporization of benzene is 85 JK^{-1} mol^{-1}. When 117 g benzene vaporizes at it's normal boiling point, calculate the entropy change of surrounding.

B-2.✍ Calculate standard entropy change in the reaction

$$Fe_2O_3\,(s) + 3H_2\,(g) \longrightarrow 2Fe\,(s) + 3H_2O\,(\ell)$$

Given : $S^o_m(Fe_2O_3, S) = 87.4$, $S^o_m(Fe, S) = 27.3$, $S^o_m(H_2, g) = 130.7$, $S^o_m(H_2O, \ell) = 69.9\ JK^{-1}\ mol^{-1}$.

B-3.✍ One mole of liquid iron at its boiling point was vaporized in an oven at 3500 K. If iron boils at 3133 K and enthalpy of vaporization is 349 KJ mol^{-1}, determine ΔS_{system}, $\Delta S_{surrounding}$ and $\Delta S_{universe}$.(Oven is considered as surroundings).

B-4. Calculate the entropy change in surroundings when 1.00 mol of $H_2O(\ell)$ is formed under standard conditions at 298 K. Given $\Delta_rH^o = -\ 286$ kJ mol^{-1}.

B-5.✍ Order of increasing of entropy among given condition of substance is :
(I) 1 mole of $H_2O(l)$ at 298 K and 0.101 M Pa
(II) 1 mole of ice at 273 K and 0.101 M Pa
(III) 1 mole of $H_2(g)$ at 298 K and 1 atm
(IV) 1 mole of $C_2H_6(g)$ at 298 K and 1 atm

B-6. Oxygen & ozone are gases at standard temperature. Their molar entropies are in the sequence $O_2 < O_3$. Using molecular properties, explain why ozone is more disordered than oxygen.

Section (C) : Free energy

C-1. What will be the states of a chemical reaction occuring at constant pressure and temperature conditions when :
(i) $\Delta G = 0$ (ii) $\Delta G > 0$ (iii) $\Delta G < 0$

C-2.✍ A gaseous reactant A forms two different product, in parallel reaction, B and C as follows :
$A \longrightarrow B;\ \Delta H^o = -3kJ,\ \Delta S^o = 20JK^{-1}$; $A \longrightarrow C;\ \Delta H^o = -3.6\ kJ,\ \Delta S^o = 10\ JK^{-1}$
Discuss the relative stability of B and C on the basis of Gibb's free energy change at 27ºC.

C-3. With the following informations, determine standard Gibb's free energy of formation of $N_2O_4(g)$.

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$ $\Delta G^o = 86.6$ kJ .....(i)

$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$ $\Delta G^o = -34.82$ kJ .....(ii)

$2NO_2(g) \longrightarrow N_2O_4(g)$ $\Delta G^o = -5.77$ kJ .....(iii)

C-4.✍ For the equilibrium : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, equilibrium constant, $K = 1.8 \times 10^{-7}$. What is $\Delta G^0$for the reaction ?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Introduction about entropy

A-1. In which state, matter have highest entropy
(A) Solid (B) Liquid (C) Gas (D) Equal in all

A-2.✍ Predict which of the following reaction (s) has a positive entropy change ?
I. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
II. $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$
III. $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$
(A) I and II (B) III (C) II and III (D) II

A-3. Mixing of non-reacting ideal gases is generally accompanied by
(A) Decrease in entropy (B) Increase in entropy
(C) Change in enthalpy (D) Increase in free energy

A-4. Which of the following reactions is associated with the most negative change in entropy ?
(A) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ (B) $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
(C) $C(s, graphite) + O_2 \longrightarrow CO_2(g)$ (D) $3C_2H_2(g) \longrightarrow C_6H_6(\ell)$

A-5. For the gas - phase decomposition, $PCl_5(g) \overset{\Delta}{\rightleftharpoons} PCl_3(g) + Cl_2(g)$:
(A) $\Delta H < 0, \Delta S < 0$ (B) $\Delta H > 0, \Delta S > 0$ (C) $\Delta H > 0, \Delta S < 0$ (D) $\Delta H < 0, \Delta S > 0$

A-6. Which one of the following has ΔS^o greater than zero.
(A) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ (B) $NaCl(aq) \rightleftharpoons NaCl(s)$
(C) $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$ (D) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

A-7.✍ For which reaction from the following, will be maximum entropy change :
(A) $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$ (B) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(C) $C(s) + O_2(g) \rightarrow CO_2(g)$ (D) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

A-8. Which of the following statement is true. The entropy of the universe
(A) Increases and tends towards maximum value
(B) Decreases and tends to be zero
(C) Remains constant
(D) Decreases and increases with a periodic rate

Section (B) : Entropy Calculation

B-1. An isolated system comprises the liquid in equilibrium with vapours. At this stage the molar entropy of the vapour is :
(A) Less than that of liquid (B) more than that of liquid
(C) Equal to zero (D) Equal to that of liquid

B-2. When two mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ heated from 300 K to 600 K at constant pressure. The change in entropy of gas (ΔS) is :

(A) $\frac{3}{2}$ R ln 2 (B) $-\frac{3}{2}$ R ln 2 (C) 5R ln 2 (D) $\frac{5}{2}$ R ln 2

B-3. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300ºC 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) $\frac{3}{2} R \ln \left(\frac{573}{473}\right)$

B-4.✍ If one mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is :

(A) zero (B) infinity (C) $\frac{5}{2}$ R ln 3 (D) R ln 3

B-5. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and ΔH = – 401.7 J mol^{-1} for the transition. Assume the surroundings to be an ice-water bath at 0ºC :

(A) – 1.09 JK^{-1} (B) 1.47 JK^{-1} (C) 0.38 JK^{-1} (D) None of these

Section (C) : Free energy

C-1. Which of the follwing is incorrect regarding Gibbs free energy

(A) it is a state function (B) it is extensive property

(C) it is macroscopic property (D) it is intensive property

C-2.✍ Which of the following conditions regarding a chemical process ensures its spontaneity at all temperature ?

(A) ΔH > 0, ΔS < 0 (B) ΔH < 0, ΔS > 0 (C) ΔH < 0, ΔS < 0 (D) ΔH > 0, ΔS < 0

C-3. When reaction in standard state is at equilibrium, then :

(A) ΔHº = 0 (B) ΔSº = 0

(C) equilibrium constant K = 0 (D) equilibrium constant K = 1

C-4. What is the free energy change (ΔG) when 1.0 mole of water at 100ºC and 1 atm pressure is converted into steam at 100ºC and 1 atm pressure ?

(A) 80 cal (B) 540 cal (C) 620 cal (D) Zero

C-5. A reaction has ΔH = – 33 kJ and ΔS = – 58 J/K. This reaction would be :

(A) spontaneous at all temperatures (B) non-spontaneous at all temperatures

(C) spontaneous above a certain temperature (D) spontaneous below a certain temperature

C-6. For a reaction $A(g) \rightleftharpoons B(g)$ at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG° of the reaction A → B is

(A) RT ℓn 4 (B) – RT ℓn 4 (C) RT log 4 (D) – RT log 4

C-7.✍ If ΔGº = – 177 K cal for (1) $2\,Fe(s) + \frac{3}{2} O_2(g) \longrightarrow Fe_2O_3(s)$

and ΔGº = – 19 K cal for (2) $4\,Fe_2O_3(s) + Fe(s) \longrightarrow 3\,Fe_3O_4(s)$

What is the Gibbs free energy of formation of $Fe_3O_4(s)$?

(A) + 229.6 kcal/mol (B) – 242.3 kcal/mol (C) – 727 kcal/mol (D) – 229.6 kcal/mol

C-8. For a paticular reaction ΔH° = – 76.6 KJ and ΔS° = 226 JK^{-1}. This reaction is :

(A) Spontaneous at all temperatures (B) Non spontaneous at all temperatures

(C) Spontaneous at temperature below 66°C (D) Spontaneous at temperature above 66°C

PART - III : MATCH THE COLUMN

1. Match the column:

	Columm-I		**Columm-II**
(A)	$(\Delta G_{system})_{T,P} = 0$	(p)	Process is in equilibrium
(B)	$\Delta S_{system} + \Delta S_{surrounding} > 0$	(q)	Process is nonspontaneous
(C)	$\Delta S_{system} + \Delta S_{surrounding} < 0$	(r)	Process is spontaneous
(D)	$(\Delta G_{system})_{T,P} > 0$	(s)	System is unable to do useful work

2.✍ Match the column :

	Columm-I		**Columm-II**
(A)	Reversible adiabatic compression	(p)	$\Delta S_{system} > 0$
(B)	Reversible vaporisation of liquid	(q)	$\Delta S_{system} < 0$
(C)	$2N(g) \longrightarrow N_2(g)$	(r)	$\Delta S_{surrounding} < 0$
(D)	$MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$	(s)	$\Delta S_{surrounding} = 0$

Exercise-2

PART - I : ONLY ONE OPTION CORRECT TYPE

1.✍ Which of the following option the first compound has less entropy than second :
(A) (i) aqueous solution of 1 M of $MgCl_2$ (ii) aqueous solution of 1 M of NaCl
(B) (i) Br_2 liquid at 25ºC (ii) Br_2 liquid at 20ºC
(C) (i) HgO solid (ii) HgS solid
(D) (i) Br_2 liquid (ii) I_2 solid

2. Isentropic process is
(A) adiabatic and irreversible process
(B) isothermal and reversible process
(C) adiabatic and reversible process
(D) isothermal and reversible for which Q = 0

3.✍ Third law of thermodynamics states that :
(A) the entropy of a perfectly crystalline pure substance at zero K is zero.
(B) absolute entropy of hydrogen ion is zero at zero K.
(C) net change in entropy in coverssion $H_{2(g)}$ (130 K) → $H_{2(g)}$ (200K) is zero.
(D) entropy generally decrease in combustion reactions.

4. Select correct statements :
S_1 : For every chemical reaction at equilibrium, standard gibbs energy of reaction is zero
S_2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing gibbs energy.
S_3 : Spontaneity is related to change in entropy of universe.
(A) S_1 S_2 S_3
(B) only S_1
(C) S_2, S_3
(D) S_1, S_3

PART - II : NUMERICAL VALUE PROBLEMS

1. The equilibrium constant for a reaction is 10. What will be the magnitude value of ΔG^o ? $R = 8.31\ JK^{-1}\ mol^{-1}$, T = 314 K. (Approximate integer value in $KJ\ mol^{-1}$)

2. For the reaction at 298 K

$$A\ (g) + B\ (g) \rightleftharpoons C\ (g) + D\ (g)$$

If $\Delta H^o = -29.8$ Kcal and $\Delta S^o = -0.1\ Kcal\ K^{-1}$ then calculate equilibrium constant (K) :

3.✍ Calculate the magnitude of free energy in $KJ\ mol^{-1}$ when 1 mole of an ionic salt MX (s) is dissolved in water at 27°C. Given
Lattice energy of MX = $780\ kJ\ mol^{-1}$
Hydration energy of MX = $-775.0\ kJ\ mol^{-1}$
Entropy change of dissolution at 27°C = $40\ J\ mol^{-1}\ K^{-1}$

4.✍ For the formation of C (g) at 300 K.

$$A\ (g) + 3\ B\ (g) \longrightarrow 2C\ (g)$$

Calculate the magnitude of ΔG^o (Kcal) if given data :

	A	B	C
ΔH_f^o (Kcal mol^{-1})	0	0	–10
ΔS_f^o (Cal K^{-1} mol^{-1})	40	30	45

5. The entropies of H_2(g) and H(g) are 60 and 50 J $mole^{-1}$ K^{-1} respectively at 300 K. Using the data given below calculate the bond enthalpy of H_2 (g) in Kcal $mole^{-1}$.

$$H_2\ (g) \longrightarrow 2H\ (g) \quad ; \quad \Delta G^o = 21.6\ KJ\ mole^{-1}$$

6. The free energy change for a reaction is –213.3 kJ mol^{-1} at 25ºC. If the enthalpy change of the reaction is –217.77 kJ $mole^{-1}$. Calculate the magnitude of entropy change for the reaction in Joule $mole^{-1}$.

7. Calculate the magnitude of standard entropy change for reaction X $\rightleftharpoons$ Y if ΔH^o = 25 KJ and K_{eq} is 10^{-7} at 300 K.

8. Calculate the magnitude of standard free energy of formation of ammonium chloride at 25ºC (approximate integer in Kcal mol^{-1}), the equation showing the formation of NH_4Cl from its elements is

$\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(s)$

For NH_4Cl, ΔH^o_f is – 313 kJ mol^{-1}, Also given that

$$S^0_{N_2} = 191.5\ JK^{-1}\ mol^{-1} \qquad S^0_{H_2} = 130.6\ JK^{-1}\ mol^{-1}$$

$$S^0_{Cl_2} = 223.0J\ K^{-1}\ mol^{-1} \qquad S^0_{NH_4Cl} = 94.6\ JK^{-1}\ mol^{-1}$$

9.✍ For the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$; ΔH = – 30 kJ to be at equilibrium at 477ºC. If standard entropy of N_2 (g) and NH_3 (g) are 60 and 50 J $mole^{-1}$ K^{-1} respectively then calculate the standard entropy of H_2(g) in $Jmole^{-1}K^{-1}$.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1.✍ In which of the following entropy increases :

(A) $Fe(s) + O_2(g) \longrightarrow Fe_2O_3(s)$.
(B) Melting of ice
(C) Crystallisation of sugar from solution
(D) Vaporisation of camphor

2.✍ When a liquid solidifies, generally, there is :

(A) Decrease in enthalpy
(B) Decrease in entropy
(C) Increase in enthalpy
(D) Increase in entropy

3. Which of the following is false about molar entropy ?

(A) It is same for all type of gases
(B) For the gas of comparable mass. It decreases with the increase in atomicity.
(C) Under identical condition, it is greater for heavier gas.
(D) For ideal gas of comparable molar mass it decreases with the increase in thermo molecular attractions.

4.✍ Which of the following statements is/are correct.

(A) Reversible adiabatic process is iso entropic process
(B) ΔS_{system} for irreversible adiabatic compression is greater than zero
(C) ΔS_{system} for free expension in zero
(D) $\Delta S_{surrounding}$ for irreversible isothermal compression is greater than zero

5.✍ The normal boiling point of a liquid `X` is 400 K. Which of the following statement is true about the process $X(l) \longrightarrow X(g)$?

(A) at 400 K and 1 atm pressure $\Delta G = 0$
(B) at 400 K and 2 atm pressure ΔG = + ve
(C) at 400 K and 0.1 atm presure ΔG = – ve
(D) at 410 K and 1 atm pressure ΔG = + ve

6. For isothermal expansion in case of an ideal gas :
(A) $\Delta H = 0$ (B) $\Delta E = 0$ (C) $\Delta G = -T.\Delta S$ (D) $T_{final} = T_{initial}$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comperhension # 1

Entropy is a state function and its value depends on two or three variables temperature (T), Pressure (P) and volume (V). Entropy change for an ideal gas having number of moles (n) can be determined by the following equation.

$$\Delta S = 2.303\ nC_V \log\left(\frac{T_2}{T_1}\right) + 2.303\ nR \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = 2.303\ nC_p \log\left(\frac{T_2}{T_1}\right) + 2.303\ nR \log\left(\frac{P_1}{P_2}\right)$$

Since free energy change for a process or a chemical equation is a deciding factor of spontaneity, which can be obtained by using entropy change (ΔS) according to the expression, $\Delta G = \Delta H - T\Delta S$ at a temperature T.

1. What would be the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 L to a volume of 50 L at 25°C [Given R = 8.3 J/mole – K]
(A) 38.23 J/K (B) 26.76 J/K (C) 20J/K (D) 28.23J/K

2. An isobaric process having one mole of ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C. What would be the molar specific heat capacity (C_V) ?
(A) $\frac{10}{\log 2}$ J/K mol (B) $\frac{10}{\log 2} - 8.3$ J/ K mol
(C) 10 × log2 J/K mol (D) 10 log2 + 8.3 J/K mol

3. For a reaction $M_2O(s) \longrightarrow 2M(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30$ kJ/mol and $\Delta S = 0.07$ kJ/K-mol at 1 atm. Calculate upto which temperature the reaction would not be spontaneous.
(A) T > 428.6 K (B) T > 300.8 K (C) T < 300.8 K (D) T < 428.6 K

Comprehension # 2

Dependence of spontaneity on temperature :

For a process to be spontaneous, at constant temperature and pressure, there must be decrease in free energy of the system in the direction of the process, i.e. $\Delta G_{P,\,T} < 0$. $\Delta G_{P,\,T} = 0$ implies the equilibrium condition and $\Delta G_{P,\,T} > 0$ corresponds to non-spontaneity.

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy changes of the process as : $\Delta G_{P,T} = \Delta H - T\Delta S$ ...(1)

The magnitude of ΔH does not change much with the change in temperature but the entropy factor $T\Delta S$ changes appreciably. Thus, spontaneity of a process depends very much on temperature.

For endothermic process, both ΔH and ΔS are positive. The energy factor, the first factor of equation, opposes the spontaneity whereas entropy factor favours it. At low temperature the favourable factor $T\Delta S$ will be small and may be less than ΔH, ΔG will have positive value indicating the nonspontaneity of the process. On raising temperature, the factor $T\Delta S$ increases appreciably and when it exceeds ΔH, ΔG would become negative and the process would be spontaneous.

For an exothermic process, both ΔH and ΔS would be negative. In this case the first factor of eq. 1 favours the spontaneity whereas the second factor opposes it. At high temperature, when $T\Delta S > \Delta H$, ΔG will have positive value, showing thereby the non-spontaneity of the process. However, on decreasing temperature, the factor $T\Delta S$ decreases rapidly and when $T\Delta S < \Delta H$, ΔG becomes negative and the process occurs spontaneously. Thus, an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.

4.✍ When $CaCO_3$ is heated to a high temperature, it undergoes decomposition into CaO and CO_2 whereas it is quite stable at room temperature. The most likely explanation of it, is
(A) The enthalpy of reaction (ΔH) overweighs the term $T\Delta S$ at high temperature.
(B) The term $T\Delta S$ overweighs the enthalpy of reaction at high temperature.
(C) At high temperature, both enthalpy of reaction and entropy change become negative.
(D) None of these.

5.✍ For the reaction at 25°C, $X_2O_4(\ell) \longrightarrow 2XO_2(g)$
$\Delta H = 2.1$ Kcal and $\Delta S = 20$ cal K^{-1}. The reaction would be
(A) spontaneous (B) non-spontaneous (C) at equilibrium (D) unpredictable

6.✍ For the reaction at 298 K, $2A + B \longrightarrow C$
$\Delta H = 100$ kcal and $\Delta S = 0.050$ kcal K^{-1}. If ΔH and ΔS are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous ?
(A) 1000 K (B) 1500 K (C) 2000 K (D) 2500 K

7.✍ A reaction has a value of $\Delta H = -40$ kcal at 400K. Above 400 K, the reaction is spontaneous, below this temperature, it is not. The values of ΔG and ΔS at 400 K are respectively.
(A) 0, – 0.1 cal K^{-1} (B) 0,100 cal K^{-1}
(C) – 10 kcal, – 100 cal K^{-1} (D) 0, – 100 cal K^{-1}

8.✍ The enthalpy change for a certain reaction at 300 K is – 15.0 K cal mol^{-1}. The entropy change under these conditions is – 7.2 cal K^{-1} mol^{-1}. The free energy change for the reaction and its spontaneous/non-spontaneous character will be
(A) – 12.84 kcal mol^{-1}, spontaneous (B) 12.84 kcal mol^{-1}, non-spontaneous
(C) – 17.16 kcal mol^{-1}, spontaneous (D) None of these

Exercise-3

*** Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

$\Delta S(A \longrightarrow C) = 50$; $\Delta S(C \longrightarrow D) = 30$; $\Delta S(B \longrightarrow D) = +20$
The entropy change for the process $A \longrightarrow B$ is **[JEE 2006, 3/184]**
(A) 100 (B) – 60 (C) – 100 (D) + 60

2. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $K = 4 \times 10^6$ at 298
$K = 41$ at 400 K
Which statements is correct ? **[JEE 2006, 3/184]**
(A) If N_2 is added at equlibrium condition, the equilibrium will shift to the forward direction because according to II^nd^ law of thermodynamics the entropy must increases in the direction of spontaneous reaction.
(B) The condition for equilibrium is $2G_{NH_3} = 3G_{H_2} + G_{N_2}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure.
(C) Addition of catalyst does not change K_p but changes ΔH.
(D) At 400 K addition of catalyst will increase forward reaction by 2 times while reverse reaction rate will be changed by 1.7 times.

3. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is :
(Given : $\Delta_rH^o_{298\,K} = -54.07$ kJ mol^{-1}, $\Delta_rS^o_{298\,K} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ JK^{-1} mol^{-1} ; $2.303 \times 8.314 \times 298 = 5705$) **[JEE 2007, 3/162]**
(A) 5 (B) 10 (C) 95 (D) 100

4. For the process $H_2O(\ell)$ (1 bar, 373 K) $\longrightarrow$ $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is : **[JEE 2007, 3/162]**

(A) $\Delta G = 0, \Delta S = +ve$ (B) $\Delta G = 0, \Delta S = -ve$ (C) $\Delta G = +ve, \Delta S = 0$ (D) $\Delta G = -ve, \Delta S = +ve$

5. **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, 3/163]**

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

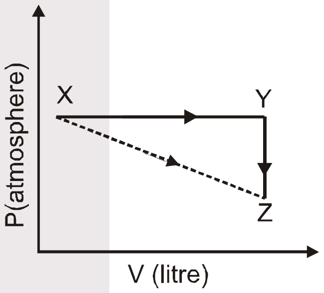
6. **Statement-1 :** There is a natural asymmetry between converting work to heat and converting heat to work.

Statement-2 : No process is possible in which the sole result is the absorption of heat form a reservoir and its complete conversion into work. **[JEE 2008, 3/163]**

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

7.* 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, 4/136]**

(A) $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$
(B) $w_{x\to z} = w_{x\to y} + w_{y\to z}$
(C) $w_{x\to y\to z} = w_{x\to y}$
(D) $\Delta S_{x\to y\to z} = \Delta S_{x\to y}$



8. For the process, $H_2O(\ell) \longrightarrow H_2O(g)$ at T = 100°C and 1 atmosphere pressure, the correct choice is : **[JEE(Advanced) 2014, 3/120]**

(A) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$ (B) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$ (D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

9. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. **[JEE(Advanced) 2015, 8/168]**

	Column-I		**Column-II**
(A)	Freezing of water at 273 K and 1 atm	(P)	q = 0
(B)	Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q)	w = 0
(C)	Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R)	$\Delta S_{sys} < 0$
(D)	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(S)	$\Delta U = 0$
		(T)	$\Delta G = 0$

10. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is : (1 L atm = 101.3 J) **[JEE(Advanced) 2016, 3/124]**

(A) 5.763 (B) 1.013 (C) –1.013 (D) –5.763

11.* For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

[JEE(Advanced) 2017, 4/122]

(A) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

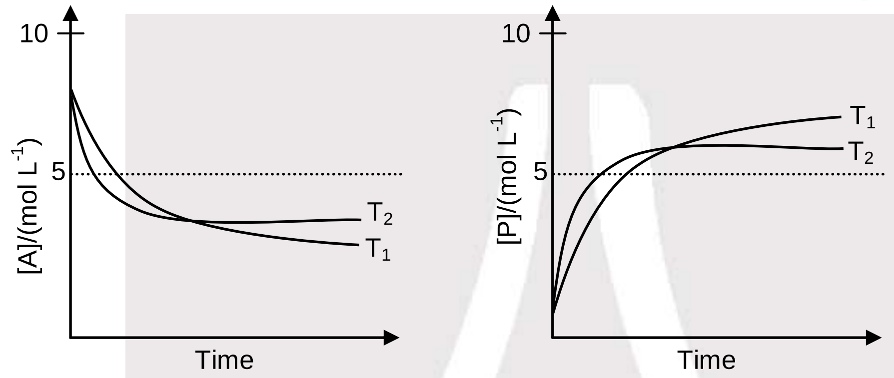
(B) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases

(C) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative

(D) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

12.* For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperature T_1 and T_2 are given below.

[JEE(Advanced) 2018, 4/120]



If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of lnK at T_1 to lnK at T_2 is greater than T_2/T_1. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(A) $\Delta H^\theta < 0, \Delta S^\theta < 0$ (B) $\Delta G^\theta < 0, \Delta H^\theta > 0$

(C) $\Delta G^\theta < 0, \Delta S^\theta < 0$ (D) $\Delta G^\theta < 0, \Delta S^\theta > 0$

13. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below :

$$2Cu(s) + H_2O(g) \longrightarrow Cu_2O(s) + H_2(g)$$

pH_2 is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln\left(p_{H_2}\right)$ is_______.

(Given: total pressure = 1 bar, R (universal gas constant) = 8 J K^{-1} mol^{-1}, ln(10) = 2.3, Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K : $2Cu(s) + \frac{1}{2}O_2(g) \longrightarrow Cu_2O(s)$; $\Delta G° = -78{,}000$ J mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta G° = -1{,}78{,}000$ J mol^{-1}; G is the Gibbs energy)

[JEE(Advanced) 2018, 3/120]

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. Identify the correct statement regarding a spontaneous process : **[AIEEE 2007, 3/120]**

(1) Exothermic processes are always spontaneous.
(2) Lowering of energy in the reaction process is the only criterion for spontaneity.
(3) For a spontaneous process in an isolated system, the change in entropy is positive.
(4) Endothermic processes are never spotaneous.

2. In conversion of lime-stone to lime, $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ the values of ΔH^o and ΔS^o are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is : **[AIEEE 2007, 3/120]**

(1) 845 K (2) 1118 K (3) 1008 (4) 1200 K

3. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. **[AIEEE 2008, 3/105]**

For the reaction, $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$ $\Delta H = -30$ kJ. To be at equilibrium the temperature will be :

(1) 500 K (2) 750 K (3) 1000 K (4) 1250 K

4. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when. **[AIEEE 2010, 4/144]**

(1) $T_e > T$ (2) $T > T_e$ (3) T_e is 5 times T (4) $T = T_e$

5. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is : **[AIEEE 2011, 4/120]**

(1) 38.3 J mol^{-1} K^{-1} (2) 35.8 J mol^{-1} K^{-1} (3) 32.3 J mol^{-1} K^{-1} (4) 42.3 J mol^{-1} K^{-1}

6. In view of the signs of Δ_rG^o for the following reactions :

$PbO_2 + Pb \longrightarrow 2PbO$, $\Delta_rG^o < 0$; $SnO_2 + Sn \longrightarrow 2SnO$, $\Delta_rG^o > 0$,

which oxidation states are more characteristics for lead and tin ? **[AIEEE 2011, 4/120]**

(1) For lead +2, for tin +2 (2) For lead +4, for tin +4
(3) For lead +2, for tin +4 (4) For lead +4, for tin +2

7. The incorrect expression among the following is : **[AIEEE 2012, 4/120]**

(1) $\frac{\Delta G_{system}}{\Delta S_{total}} = -T$ (2) In isothermal process, $w_{reversible} = -nRT \ln \frac{V_f}{V_i}$

(3) $\ln K = \frac{\Delta H^o - T\Delta S^o}{RT}$ (4) $K = e^{-\Delta G^o/RT}$

8. The following reaction is performed at 298 K.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K ? ($K_P = 1.6 \times 10^{12}$) **[JEE(Main) 2015, 4/120]**

(1) R(298) in (1.6×10^{12}) – 86600 (2) 86600 + R(298) ln (1.6×10^{12})

(3) $86600 - \frac{\ln(1.6 \times 10^{12})}{R\,(298)}$ (4) 0.5 [2 × 86,600 – R (298) ln (1.6×10^{12})]

9. The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25ºC; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be : (R = 8.314 JK^{-1} mol^{-1}) **[JEE(Main) 2018, 4/120]**

(1) 3260 (2) –3267.6 (3) 4152.6 (4) –452.46

JEE-MAIN ONLINE PROBLEMS

1. The molar heat capacity (C_p) of CD_2O is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of CD_2O vapour from 1000 K to 100 K at constant pressure will be : (D = deuterium, at. mass = 2 u) **[JEE(Main) 2014 Online (11-04-14), 4/120]**

(1) 23.03 cal deg^{-1} (2) – 23.03 cal deg^{-1} (3) 2.303 cal deg^{-1} (4) – 2.303 cal deg^{-1}

2. Then entropy (S^o) of the following substances are :

$CH_4(g)$ 186.2 JK^{-1} mol^{-1}, $O_2(g)$ 205.0 JK^{-1} mol^{-1}

$CO_2(g)$ 213.6 JK^{-1} mol^{-1}, $H_2O(\ell)$ 69.9 JK^{-1} mol^{-1}

The entropy change (ΔS^o) for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$ is :

[JEE(Main) 2014 Online (12-04-14), 4/120]

(1) –312.5 JK^{-1} mol^{-1} (2) –242.3 JK^{-1} mol^{-1} (3) –108.1 JK^{-1} mol^{-1} (4) –37.6 JK^{-1} mol^{-1}

3. For the reaction, A(g) + B(g) → C(g) + D(g), ΔH^o and ΔS^o are, respectively, –29.8 kJ mol^{-1} and –0.100 kJ K^{-1} mol^{-1} at 298 K. The equilibrium constant for the reaction at 298 K is:
[JEE(Main) 2016 Online (09-04-16), 4/120]
(1) 1 (2) 10 (3) 1.0×10^{-10} (4) 1.0×10^{10}

4. A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement about the reaction among the following:
[JEE(Main) 2016 Online (09-04-16), 4/120]
(1) Both ΔH and ΔS are positive. (2) ΔH is negative while ΔS is positive.
(3) ΔH is positive while ΔS is negative. (4) Both ΔH and ΔS are negative.

5. $\Delta_f G^\circ$ at 500 K for substance 'S' in liquid state and gaseous state are +100.7 kcal mol^{-1} and +103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to :
(R = 2 cal K^{-1} mol^{-1}) **[JEE(Main) 2018 Online (15-04-18), 4/120]**
(1) 0.1 atm (2) 1 atm (3) 10 (4) 100 atm

6. Given
(i) $2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$; $\Delta_r G^\circ = + 1487.0$ kJ mol^{-1}
(ii) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$; $\Delta_r G^\circ = -514.4$ kJ mol^{-1}
Free energy change, $\Delta_r G^\circ$ for the reaction $2Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g)$ will be
[JEE(Main) 2018 Online (15-04-18), 4/120]
(1) –112.4 kJ mol^{-1} (2) –56.2 kJ mol^{-1} (3) –168.2 kJ mol^{-1} (4) –208.0 kJ mol^{-1}

7. For which of the following processes, ΔS is negative ? **[JEE(Main) 2018 Online (16-04-18), 4/120]**
(1) C(diamond) → C(graphite) (2) N_2(g, 1 atm) → N_2(g, 5 atm)
(3) N_2(g, 273 K) → N_2(g, 300 K) (4) $H_2(g) \rightarrow 2H(g)$

8. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is: (Specific heat of water liquid and water vapour are 4.2 kJ $K^{-1}kg^{-1}$ and 2.0 kJ K^{-1} kg^{-1}; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively). (log 273 = 2.436, log 373 = 2.572, log 383 = 2.583) **[JEE(Main) 2019 Online (09-01-19), 4/120]**
(1) 8.49 kJ kg^{-1} K^{-1} (2) 9.26 kJ kg^{-1} K^{-1} (3) 2.64 kJ kg^{-1} K^{-1} (4) 7.90 kJ kg^{-1} K^{-1}

9. A process has ΔH = 200 J mol^{-1} and ΔS = 40 JK^{-1} mol^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous :
[JEE(Main) 2019 Online (10-01-19), 4/120]
(1) 5 K (2) 12 K (3) 4 K (4) 20 K

10. The process with negative entropy change is: **[JEE(Main) 2019 Online (10-01-19), 4/120]**
(1) Sublimation of dry ice
(2) Dissolution of iodine in water
(3) Dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(4) Synthesis of ammonia from N_2 and H_2

11. Two blocks of the same metal having same mass and at temperature T_1 and T_2, respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is: **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) $2C_P \ln\left(\frac{T_1+T_2}{4T_1T_2}\right)$ (2) $2C_P \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$

(3) $C_P \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$ (4) $2C_P \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$

12. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as $\Delta_rG°$(in kJ mol^{-1}) = $120 - \frac{3}{8}T$. The major component of the reaction mixture at T is :

[JEE(Main) 2019 Online (11-01-19), 4/120]

(1) Y is T = 280 K (2) Y is T = 300 K (3) X if T = 315 K (4) X if T = 350 K

13. The standard reaction Gibbs energuy for a chemical reaction at an absolute temperature T is given by $\Delta G° = A - BT$, where A and B are non-zero constants. Which of the following is TRUE about this reaction ? **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) Endothermic if A > 0 (2) Exothermic if B < 0

(3) Exothermic if A > 0 and B < 0 (4) Endothermic if A < 0 and B > 0

14. For the equilibrium $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of $\Delta G°$ at 298 K is approximately :

[JEE(Main) 2019 Online (11-01-19), 4/120]

(1) 80 kJ mol^{-1} (2) –100 kJ mol^{-1} (3) –80 kJ mol^{-1} (4) 100 kJ mol^{-1}

15. The reaction, $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_rH° = +491.1$ kJ mol^{-1} and $\Delta_rS° = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is:

[JEE(Main) 2019 Online (11-01-19), 4/120]

(1) 2380.5 K (2) 1890.0 K (3) 2040.5 K (4) 2480.3 K

Answers

EXERCISE - 1

PART – I

A-1. Because larger space creates more disorder.

A-2. Dissolution of solute makes the motion of solute particles free. Also the increased number of particles in mixed state increases disorderness.

A-3. (a) ΔS_{sys} is positive; ΔS_{surr} is negative, (b) ΔS_{sys} is positive; ΔS_{surr} is negative;
(c) ΔS_{sys} is positive; ΔS_{surr} is negative.

A-4. Entropy of the universe is constantly increasing. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$ for a spontaneous process.

A-5. At 0 K, entropy of a perfect crystalline pure substance is taken to be zero.

A-6. $\Delta G_{T,P} = (-)$ve or $\Delta S_{total} > 0$

A-7. $\Delta G = \Delta H - T\Delta S$
For spontaneous reaction $\Delta G = (-)$ ve
$\therefore$ ΔS Should be positive

B-1. -1.5×85 J/K

B-2. -215.2 JK^{-1} mol^{-1}

B-3. $\Delta S_{system} = 111.4$ JK^{-1}, $\Delta S_{surr} = -99.71$ JK^{-1}, $\Delta S_{univ} = +11.69$ JK^{-1}

B-4. Entropy change in surroundings = 959.73 JK^{-1}.

B-5. II < I < III <IV

B-6. Ozone has three atoms per molecule, whereas O_2 has only two.

C-1. (i) Chemical reaction in equilibrium state (ii) non-spontaneous (iii) Spontaneous.

C-2. ΔG^o indicates that B is more stable than C.

C-3. 97.79 kJ

C-4. ΔG^o of reaction is 38477 J/mol.

PART - II

A-1.	(C)	**A-2.**	(C)	**A-3.**	(B)	**A-4.**	(D)	**A-5.**	(B)
A-6.	(C)	**A-7.**	(B)	**A-8.**	(A)	**B-1.**	(B)	**B-2.**	(C)
B-3.	(C)	**B-4.**	(D)	**B-5.**	(C)	**C-1.**	(D)	**C-2.**	(B)
C-3.	(D)	**C-4.**	(D)	**C-5.**	(D)	**C-6.**	(A)	**C-7.**	(B)
C-8.	(A)								

PART - III

1. (A) → (p, s); (B) → (r) ; (C) → (q, s) ; (D) → (q, s).

2. (A) → (s); (B) → (p, r); (C) → (q); (D) → (p, r)

EXERCISE – 2

PART - I

1.	(C)	**2.**	(C)	**3.**	(A)	**4.**	(C)

PART - II

1.	6	**2.**	1	**3.**	7 kJ mol^{-1}.	**4.**	8	**5.**	8
6.	15	**7.**	51	**8.**	48	**9.**	40		

PART - III

1.	(BD)	**2.**	(AB)	**3.**	(ABD)	**4.**	(ABD)	**5.**	(ABC)
6.	(ABCD)								

PART - IV

1.	(A)	**2.**	(B)	**3.**	(D)	**4.**	(B)	**5.**	(A)
6.	(C)	**7.**	(D)	**8.**	(A)				

EXERCISE – 3

PART - I

1.	(D)	**2.**	(B)	**3.**	(B)	**4.**	(A)	**5.**	(D)
6.	(A)	**7.**	(AC)	**8.**	(B)				
9.	(A-R,T); (B-P,Q,S); (C-P,Q,S); (D-P,Q,S,T)					**10.**	(C)	**11.**	(AB)
12.	(AC)	**13.**	–14.6						

PART - II

JEE-MAIN OFFLINE PROBLEMS

1.	(3)	**2.**	(2)	**3.**	(2)	**4.**	(2)	**5.**	(1)
6.	(3)	**7.**	(3)	**8.**	(4)	**9.**	(2)		

JEE-MAIN ONLINE PROBLEMS

1.	(2)	**2.**	(2)	**3.**	(1)	**4.**	(1)	**5.**	(1)
6.	(2)	**7.**	(2)	**8.**	(2)	**9.**	(1)	**10.**	(4)
11.	(3)	**12.**	(3)	**13.**	(1)	**14.**	(1)	**15.**	(4)