# CHEMICAL THERMODYNAMICS & ENERGETICS

## SYNOPSIS

- Thermodynamics means flow of heat
- It deals with the quantitative relation between heat and other form of energy
- The thermodynamic laws are based on experimental facts but not theoretical facts
- The law predicts feasibility of a reaction and energy transformation in the process
- It does not give any information about rates of the process
- Thermodynamics is limited to macro systems
- System : The part of the universe having definite bounderies, real or imaginary which is under thermodynamic study or investigation.
- Surroundings : The rest of the universe which is not under thermodynamic study

Universe = System + Surrounding

- The real or imaginary line which separates system and surroundings is called **Boundary**

**Classification of systems :** (on exchange of energy & matter between system and surroundings)

1) Open system : Both energy and matter can be exchanged between the system and surrounding (neither sealed nor insulated)

Ex : hot water in a vessel without lid

2) Closed system : Energy alone is exchanged between system and surroundings but not the matter (sealed but not insulated)

Ex :- hot water in a closed container

**Isolated system :** Neither energy nor matter is exchanged between system and surroundings (sealed and insulated)

Ex : - Coffee in thermosflask

**First law of thermodynamics**

* This is also called "law of conservation of energy"
* According to this energy can neither be created nor be destroyed but can be transformed from one form to another
* According to first law the total energy of system and the surroundings is constant or conserved
* The first law of thermodynamics rules out the possibility of construction of a perpetual motion machine
* Aperpetual motion machine is one which is operating in cycles, can produce work with out any expenditure of energy on it

**Mathematical representation of first law**

$\Delta V = q + w$
$\Delta U$ = change in interval energy
q = heat supplied to the system
w = work done on the system

According to IUPAC conventions

1) heat absorbed by the system (+ve)
2) heat released by the system (– ve)
3) workdone by the system (– ve)
4) workdone on the system (+ve)

**Internal Energy : (E or V)** The energy stored in a substance at constant temperature and pressure is called internal energy (or) Intrinsic energy The energy change taking place at constant volume is known as internal energy change ($\Delta E$)

**Measurable properties or state variables of a system**

**Ex.** 1) Pressure 2) Volume 3) Temperature 4) Concentration

The state of a system is defined if its state variables are defined

**State function :** Its magnitude depends only on the state of the system but not on the path in which the state is reached

Ex : - Internal energy , enthalpy, Free energy, Entropy

**Path functions :** Whose value depends on the path of the system by which the state is reached

Ex : – Heat (Q) and Work (W)

**Heat capacity (H) (or ) Enthalpy**

The total heat content of a system at constant pressure and temperature is known as heat capacity (or) Enthalpy

The energy change taking place at constant pressure and temperature is known as Enthalpy change (ΔH)

If the heat change takes place at constant volume, no mechanical work is done (W = O)

$\Delta E_V = Q_V$ ( $\because$ W = O)

If the process is carried out at constant pressure , volume change takes place

$\Delta E = Q_P - PdV$

(or) $Q_P = \Delta E + PdV = \Delta H$

Enthalpy of a system is state function .

The quantity of heat exchanged at constant pressure is less than that exchanged at constant volume . The difference amount is utilised for doing expansion work

**Limitations of 1st law of Thermodynamics**

1) 1st law does not indicate the direction in which a process occur (or) feasibility (or) Spontaneity of the process

2) It does not predict, extent of conversion of energy from one form to other, in the process or transformation

**Examples explaining the limitations of 1st law**

i) Heat flows from higher temperature end to lower temperature end in a non- uniformly heated rod

ii) Water flows from higher level to lower level

iii) Gas flows from higher pressure region to lower pressure region.

The above are some examples of spontaneous processes

**Spontaneous process**

A process which occurs on its own without the intervention of any external agency of any kind

All naturally occurring processes are spontaneous

All spontaneous (or) natural process are thermodynamically irreversible

**Second law of thermodynamics**

To overcome the limitations in1st law, 2nd law of thermodynamics is introduced

**Statements of second law of thermodynamics**

1) It is impossible to construct a machine working in cycles which transforms heat from a lower temperature region to higher temperature region without the intervention of any external agency

A machine which transforms heat from lower temperature region to higher temperature region on its own is called “perpetual motion machine of second kind”

2) Heat cannot flow from a colder body to a hotter body on it’s own

3) Heat cannot be converted into work completely without causing some permanent changes in the system involved or in the surroundings

4) All spontaneous process are thermodynamically irreversible and entropy of the system increases in all spontaneous processes

**ENTROPY**: Introduced by CLAUSIUS

- Entropy means transformation. In is denoted by the letter 'S'
- It is the measure of disorder or randomness of the system
- The greater the disorder, the greater will be the entropy of the system.
- It is a statefunction.
- Entropy change

  $q_{rev}$ = Heat absorbed by the system reversibly at temperature 'T' during state change.
- S gas > S $_{\text{liquid}}$ > S $_{\text{solid}}$ for a given substance.
- For a spontaneons process in an isolated system, the total entropy change is positive .
- For a non-isolated system entropy change $\Delta S_{total} = \Delta S_{Systems} + \Delta S_{Surroundings}$
- For a spontaneons process ΔS $_{\text{total}}$ is positive $\Delta S_{total} = \left(\Delta S_{system} + \Delta S_{surroundings}\right) > 0$
- In exothermic reaction heat released by the reactions increases the disorder of the surroundings and overall entropy change is positive
- In endothermic reactions heat flows from the surroundings into the system hence the entropy of surroundings decreases and entropy of the system increases. $\Delta S_{fusion} = \frac{\Delta H^0_{fusion}}{T}$ $\Delta G = \Delta H_{(sys)} - T\Delta S_{(sys)}$ $\Delta S = \frac{q_{rev}}{T}$ $+ S\Delta T_{(sys)}$
- If r + ve, the change is spontaneous.

**Entropy change during phase transformations:**

- 
- $\Delta S_{vapourisition} = \frac{\Delta H^0{}_{vapourisation}}{T}$

**Gibb's Energy (G):**

$\Delta H$ negative is a required condition but not a necessary and sufficient condition for the spontaneity of a process ( or ) reaction.

positive is a required condition but not necessary and sufficient condition for the spontaneity of a process ( or) reaction.

There are some reactions which are spontaneous even when = + ve; ( or ) = - ve.

A new thermodynamic function is introduced by Gibbs involving both enthalpy and entropy functions known as " free energy function" (G) to explain the spontaneity of the reaction

'G' is referred as Gibb's energy ( or) Gibb's function

G = H - T S

(i) For Isothermal change $\Delta T = 0$

$$(\text{ or})\ \Delta G = \Delta H - T\Delta S$$

(ii)

For a spontaneous process $\Delta S$ is positive

by knowing the spontaneity of a process can be predicted.

= negative for spantaneous reactions

= positive for non-spontaneous reactions

= zero for equilibrium reactions

Relation between spontaneity of a reaction and the algebric signs of , , and T.

| | | | Nature of reaction |
|---|---|---|---|
| - | + | - | spontaneous at all 'T' values |
| + | - | + | non-spontaneous at all 'T' values |
| - | - | - | spontaneous at low 'T' values |
| - | - | + | non-spontaneous at high 'T' values |
| + | + | + | non-spontaneious at low 'T' values |
| + | + | - | spontaneous at high 'T' values |

$$\Delta G^0 = -RT\ln K \quad \Delta G = -T\Delta S_{(total)} \quad \lim_{T\to 0} S_{(sys)} = 0 \quad S_T = \int_0^T \frac{C_p}{T}.dT \quad -T\Delta S_{(sys)}$$

High temperature is a relative term. The reference here is the equilibrium temperature i.e. temperature at which .

Relation between $^0$( standard free energy ) and 'K' ( equilibrium constant)

$$= -2.303RT\log K$$

- Many reactions occur in industry, metallurgy and biosystems with as negative value.
- These reactions occur as they are coupled with reactions of large negative values.
- Non spontaneous reactions at low temperature are made spontaneous at high temperature.

**Third law of thermodynamics:**

- According to Max Plank the entropy of a pure and perfectly crystalline substance is zero at absolute zero temperature ( - 273$^0$C )
- Third law of thermodynamics is also referred as Nernst heat theorem
- Third law of thermodynamics does not lead to any new concept of thermodyunamics unlike the Ist law and the second law. It only imposes a limitation on the value of entropy.

- Entropy (S) of a substance at any temperature is calculated if the temperature dependance of $C_p$ is known in evaluating the absolute value of entropy of any substance.
- Accurate determination of entropy ( $S_T$) requires the heat capacity at constant pressure ( $C_p$).
- At absolute zero ( or ) around absolute zero $C_p$ can not be measured.
- $C_v$ ( heat capacity at constant volume ) value is obtained by using extrapolating technique and the Debye equation.

  $C_v = aT^3$

  a = constant for a substance.
- At, the temperature in the vicinity of absolute zero ( $C_p$-$C_v$) is negligible. Hence $C_p = C_v$

  Hence absolute entropy ( $S^0$) is calculated using $C_v$ value
- Absolute entropy values of some substances at 298K and 1 atm.

| | |
|---|---|
| C ( graphite ) | 5.7 $JK^{-1}mol^{-1}$ |
| C ( dimond ) | 2.4 |
| C ( gas ) | 198 |
| S ( Rhombic ) | 31.7 |
| $H_2$ ( gas ) | 130.6 |
| $N_2$ ( gas ) | 191.5 |
| $O_2$ ( gas ) | 205.1 |
| $H_2O$ ( liquid ) | 69.9 |
| $H_2O$ ( gas ) | 188.8 |

for a general reaction

$aA + bB \longrightarrow cC + dD$

is given by

$$\Delta S^0 = (cS_C^0 + dS_D^0) - (a.S_A^0 + bS_B^0)$$

= total entropy of produdcts - total entropy of reactants

$S^0$ 's are molar entropies.

## CONCEPTUAL QUESTIONS
## LEVEL - I

1. Thermodynamic laws speak about
1) rates of chemical changes
2) feasibility and energy transformations of a process
3) Both the rate and energy changes of a process
4) Energy changes in chemical reactions only

2. The object under thermodynamical study is called
1) System
2) Universe
3) Surrounding
4) Boundary

3. Which of the following are true about a "system"
1) Will have definite amount of substance
2) Energy and matter may or may not be exchanged with surroundings
3) Universe -surroundings
4) All of the above

4. Hot water in a thermos flask is an example for
1) Isolated system
2) Open system
3) Closed system
4) Adiabatic system

5. In open system, system and surroundings exchange
1) Energy only
2) Matter only
3) Energy and matter
4) None

6. In a closed system
1) Energy is not exchanged
2) Matter is exchanged
3) Energy is only exchanged
4) Energy and malter are exchanged

7. "Closed system" is
1) Perfectly sealed
2) Perfectly insulated
3) Both perfectly insulated and sealed
4) Neither insulated nor sealed

8. In a open system
1) Energy is exchanged with surroundings
2) Matter is exchanged with surroundings
3) Both energy and mater are exchanged with surroundings
4) Neither energy nor matter are exchanged

9. First law of Thermodynamics is also known as
1) Law of conservation of energy
2) Law of conservation of mass
3) Law of multiple proportions
4) None

10. According to 1st law of Thermodynamics
1) Energy can be created but not destroyed
2) Energy cannot be created but can be destroyed
3) Energy can be created and destroyed
4) Energy can not be created nor destroyed

11. Which of the following statement is true about 1st law of Thermodynamics
1) Energy is neither created nor destroyed
2) If particular form of energy disappears the equivalent quantity appears in another form
3) It is impossible to construct a perpetual motion machine of 1st kind
4) All are true

12. The perpetual motion machine is
1) Can't produce energy unless energy is consumed
2) Can produce energy without expenditure of energy on it
3) Do not obey 1st law of Thermodynamics
4) Both 2 and 3

13. According to 1st law of Thermodynamics
1) The energy of system is constant
2) The energy of universe is constant
3) The energy of surroundings is constant
4) The energy of system and surroundings are not constant

14. Mathematical representation of 1st law
1) $Q = \Delta E + W$
2) $\Delta H = \Delta E + P\Delta V$
3) $W = Q \times \Delta E$
4) All

15. The correct IUPAC convention
1) Heat gained by system +ve sign
2) Work done by system – ve sign
3) Work done by system +ve sign
4) Both 1 and 2

16. Energy hidden in a definite quantity of substance
1) Enthalpy
2) Internal energy
3) Free energy
4) Any of the above

17. 1st law cannot explain
1) Spontaneity of process
2) Extent of conversion of energy from one form to other
3) Perpepual machine of 1st kind
4) All of the above

18. All natural processes are
1) Spontaneous
2) non - spontaneous
3) Exothermic
4) Endothermic

19. Which of the following process(es) are non-spontaneous
1) Heat flow from hot end to cool end
2) Water flow from higher level to lower level
3) Gas flow from lower pressure region to higher pressure region
4) All

20. Machine which transfers heat from lower temperature region two higher temperature region on its own without the interference of any external agency is
1) Perpetual motion machine of 1st kind
2) Perpetual motion machine of 2nd kind
3) Perpetual motion machine of 3rd kind
4) None

21. The statement "Heat cannot flow from colder body to hotter body" is known as
1) 1st law of Thermodynamics
2) Zeroth law
3) 2nd law of Thermodynamics
4) Law of conservation of energy

22. Which statement is true about 2nd law of Thermodynamics
1) Heat cannot be converted to into work without changes in system or surroundings
2) It is impossible to construct a perpetual motion machine of second kind
3) All spontaneous process are thermodynamically irreversible
4) All are true

23. "Entropy of a system increases in all spontaneous process " known as
1) 1st law of Thermodynamics
2) 2nd law of Thermodynamics
3) Zeroth law 4) 3rd law of Thermodynamics

24. 'Energy of Universe is conserved but entropy of Universe always increases during any natural process'. The statement is based on
(1) Faradays laws
(2) 3rd law of thermodynamics
(3) 1st and 2nd law of thermodynamics
(4) Zeroth law of thermodynamics

25. The relationship between enthalpy change and internal energy change for a system is given by
(1) (2)
(3) (4)

26. At absolute zero, the entropy of a perfect crystal is zero, this is
(1) Zeroth Law of thermodynamics
(2) 1st Law of thermodynamics
(3) 2nd Law of thermodynamics
(4) 3rd Law of thermodynamics

27. All the naturally occurring processes proceed spontaneously in a direction which leads to
(1) Increase in enthalpy of system
(2) Decreases in entropy of system
(3) Increase in entropy of system
(4) Increase in entropy of Universe

## KEY

| | | | |
|---|---|---|---|
| 1) 2 | 2) 1 | 3) 4 | 4) 1 |
| 5) 3 | 6) 3 | 7) 1 | 8) 3 |
| 9) 1 | 10) 4 | 11) 4 | 12) 4 |
| 13) 2 | 14) 1 | 15) 4 | 16) 2 |
| 17) 4 | 18) 1 | 19) 3 | 20) 2 |
| 21) 3 | 22) 4 | 23) 2 | 24) 3 |
| 25) 1 | 26) 4 | 27) 4 | |

## ENTROPY

1. Entropy is a measure of
1) disorder 2) internal energy
3) efficiency
4) useful work done by the system

2. The Entropy of the universe
1) tends towards a maximum
2) tends towards a minimum
3) tends to zero 4) remains constant

3. Which of the following has highest Entropy
1) Mercury 2) Hydrogen
3) Water 4) Graphite

4. Entropy change for an adiabatic reversible process is

$(\Delta H)$ $(\Delta E)$ $\Delta H = \Delta E + P\Delta V$ $\Delta H = \Delta E + RT$

1) zero 2) +ve
3) – ve 4) negative or zero

5. Which of the following statements is incorrect
1) The entropy of an isolated system increases in an irreversible process
2) The entropy of an isolated system remains unchanged in a reversible process
3) $\Delta S_{system}$ as well as $\Delta S_{Surrounding}$ are negative quantities
4) Entropy can never decrease

6. In which of the following cases, the reaction is spontaneous at all temperature
1) $\Delta H > 0, \Delta S > 0$ 2) $\Delta H < 0, \Delta S > 0$
3) $\Delta H < 0, \Delta S < 0$ 4) $\Delta H > 0, \Delta S < 0$

7. For an endothermic reaction, ΔS is positive the reaction is
1) feasible when $T\Delta S > \Delta H$
2) feasible when $\Delta H > T\Delta S$
3) feasible at all temperatures
4) not feasible at all

8. When potassium chloride is dissolved in water
1) Entropy increases
2) Entropy decreases
3) Entropy increases and then decreases
4) Free energy increases

9. For a reversible process at equilibrium, the change in entropy may be expressed as

1) 　　2) $\Delta S = \frac{q_{rev}}{T}$

3) $\Delta S = \frac{-\Delta H}{T}$　　4) $\Delta S = \Delta G$

10. When solid changes into liquid, the entropy

1) increases　　2) remains the same

3) decreases　　4) becomes zero

11. Which of the following processes is accompanied by decrease inentropy ?

1) Evaporation of water

2) Sublimation of dry ice

3) Melting of ice

4) Condensing steam

12. The units of entropy are

1) J $mol^{-1}$　　2) $JK^{-1}$ $mol^{-1}$

3) $Jg^{-1}$　　4) $JKmol^{-1}$

13. Find the entropy change for the conversion of 1 mole of $\alpha$ – tin (at $13^0$C, 1 atm) to 1 mole of $\beta$ – tin ($13^0$C, 1 atm) if the enthalpy of transition is 2.095KJ $mol^{-1}$

1) 7.32 J $mol^{-1}$ $K^{-1}$　　2) 14.62 $JK^{-1}$ $mol^{-1}$

3) 56. J $mol^{-1}$ $K^{-1}$　　4) 0

14. $\Delta H$ (vap) for water is 40.7 KJ $mol^{-1}$. The entropy of vapourisation of water is

1) – 40.7 KJ $mol^{-1}$ $K^{-1}$　　2) 407 J $mol^{-1}$ $K^{-1}$

3) 109 J $mol^{-1}$ $K^{-1}$　　4) 722 J $mol^{-1}$

15. The following data is known about the melting of a compound AB. $\Delta H = 9.2$ KJ $mol^{-1}$ $\Delta S = 0.008$ KJ $K^{-1}$ $mol^{-1}$. It s melting point is

1) 736K　　2) 1050K

3) 1150K　　4) $1150^0$C

16. For the process

1) Both $\Delta H$ and $\Delta S$ are +ve

2) $\Delta H$ is – ve, $\Delta S$ is +ve

3) $\Delta H$ is +ve, $\Delta S$ is – ve

4) Both $\Delta H$ and $\Delta S$ are – ve

17. One mole of ice is converted into water at 273k. The entropies of $H_2O_{(s)}$ and $H_2O_{(l)}$, are 38.20 and 60.01 J.$mol^{-1}$ $K^{-1}$ respectively The enthalpy change for the conversion is

1) 59.54 J $mol^{-1}$　　2) 5954 J $mol^{-1}$

3) 595.4 J $mol^{-1}$　　4) 320.6 J.$mol^{-1}$

18. For a process spontaneous at all conditions of temperature which of the following is true?

(1) $\Delta S$ positive and　　positive

(2)　　positive and　　negative

(3)　　negative and　　positive

(4)　　negative and　　negative

19. A reaction will never be spontaneous at any temperature and pressure provided.

(1)　　positive and　　positive

(2)　　positive and　　negative

(3)　　negative and　　positive

(4)　　negative and　　negative

20. For a spontaneous process, which of the following is true?

(1)　　positive　　(2)　　positive

(3)　　positive　　(4)　　negative

21. Which of the following reaction is attended by an increase in entropy?

(1) $N_2(g) + 3H_2(g)$　　$2NH_3(g)$

(2) $2H_2(g) + O_2(g)$　　$2H_2O(l)$

(3) $H_2(g) + I_2(g)$　　$2HI(g)$

(4) C(graphite) + $H_2O(g)$　　$CO(g) + H_2(g)$

22. For the reaction, 2HgO(g)　　$2Hg(l) + O_2(g)$

(1)　　(2)

$\Delta H < 0$ & $\Delta S > 0$ $_{sol}$ $_{total}$ $_{2(s)}$ $q_{rev}$ $_{2(g)}$

(3)　　(4)

23. The direction of chemical reaction at constant temperature and pressure is the direction of increase of

(1) Entropy of the system

(2) Gibb's free energy of the system

(3) Enthalpy of the system

(4) None of these

24. For a non-spontaneous reaction, at 30°C, . The reaction becomes spontaneous, by

(1) Decreasing temperature

(2) Increasing temperature

(3) Maintaining temperature constant

(4) None of these

25. Which state has minimum randomness?

(1) Steam

(2) Liquid water

(3) Crystal ice

(4) All have same randomness

26. The value of is negative for the process
    (1) Burning of rocket fuel
    (2) Dissolution of sugar
    (3) Sublimation of iodine
    (4) Freezing of water

27. The quantity which is not zero for an element in its standard state at 298 K is
    (1) S°  (2) H°
    (3) G°  (4) Both H° and S°

28. Thermodynamic parameter which is a state function and is also used to measure disorder of the system is
    (1) Entropy  (2) Fugacity
    (3) Viscosity  (4) Periodicity

29. The most random state of $H_2O$ system is
    (1) Ice
    (2) $H_2O(l)$ at 80°C; 1 atm
    (3) Steam
    (4) $H_2O(l)$ at 25°C; 1 atm

30. For which of the following process is > 0?
    (1) $MgCO_3(s)$ $MgO(s) + CO_2(g)$
    (2) $2I(g)$ $I_2(g)$
    (3) $Na^+(g) + Cl^-(g)$ $NaCl(s)$
    (4) $H_2O(l)$ $H_2O(s)$

31. Which of the following process involves decrease in the entropy of system?
    (1) $Br_2(l)$ $Br_2(g)$
    (2) Diamond to graphite
    (3) $N_2(g)$ 10 atm $N_2(g)$ 1 atm
    (4) Boiling of egg so that it become hard

32. In which of the following process entropy increases?
    (a) Rusting of iron
    (b) Vapourisation of Camphor
    (c) Crystallisation of sugar from syrup
    (d) Atomisation of dihydrogen
    (1) (a) and (b)  (2) (b) and (c)
    (3) (b) and (d)  (4) Only (d)

33. What is true about entropy?
    (1) Entropy of Universe increases and tends towards maximum value
    (2) Entropy of Universe decreases and tends to be zero
    (3) Entropy of Universe always remain constant
    (4) Entropy increases and decreases with a periodic rate

34. For the spontaneous process 2F(g) $F_2(g)$, the sign of and respectively are
    (1) +, –  (2) +, +
    (3) –, –  (4) –, +

35. Entropy of a perfect crystalline solid at absolute zero is
    (1) Zero  (2) Less than zero
    (3) Greater than zero
    (4) Depends upon nature of the solid

**KEY**

| | | | |
|---|---|---|---|
| 1) 1 | 2) 1 | 3) 2 | 4) 1 |
| 5) 3 | 6) 2 | 7) 1 | 8) 1 |
| 9) 2 | 10) 1 | 11) 4 | 12) 2 |
| 13) 2 | 14) 3 | 15) 3 | 16) 1 |
| 17) 2 | 18) 2 | 19) 3 | 20) 3 |
| 21) 4 | 22) 2 | 23) 1 | 24) 2 |
| 25) 3 | 26) 4 | 27) 1 | 28) 1 |
| 29) 3 | 30) 1 | 31) 4 | 32) 3 |
| 33) 1 | 34) 3 | 35) 1 | |

## GIBBS ENERGY

1. Which among the following are required conditions but not necessary and sufficient conditions spontaneous reactions
   1) ΔH = – ve only  2) ΔS = + ve only
   3) Both ΔH = – ve and ΔS = +ve
   4) neither ΔH = – ve nor ΔS = +ve

2. Which of the following relations is not correct
   1) G = H – TS
   2) $\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$
   3) $T\Delta S_{system} = \Delta H_{system} - \Delta G_{system}$
   4) $\Delta H_{system} = \Delta G_{system} - T\Delta S_{system}$

$\Delta S$ $-\frac{RT}{\Delta G^0}$

3. For a spontaneous process
   1) $\Delta G_{system} = +ve_{only}$
   2) $\Delta G_{system} = -$ ve only
   3) $\Delta S_{total} = +ve$
   4) both 2 & 3

4. Which of the following is incorrect
   1) When ΔG < 0 process is spontaneous
   2) When ΔG > 0 process is nonspontaneous
   3) When ΔG = 0 process is at equilibrium
   4) When ΔG > 0 process is spontaneous

5. Which of the following conditions make the process non spontaneous at all temperatures
   1) ΔH = +ve ; ΔS = –ve
   2) ΔH = – ve ; ΔS =– ve
   3) ΔH = +ve ; ΔS = +ve
   4) ΔH = + ve ; ΔS = +ve

6. Gibs - Helmholtz equation
   1) G= H–T S  2) G= H– S
   3) G = T H–T S  4) ΔG = T H – S

7. Gibbs energy change G is related to equilibrium constant ‘K’ as
   1) $G^0 = -RTLnK$  2) $G^0 = RTLnK$
   3) LnK =  4) $LnK = \frac{\Delta G^0}{RT}$

8. $\Delta S_{surroundings} = +959.1\ JK^{-1}\ mol^{-1}$

$S_{system} = -163.1\ JK^{-1}\ mol^{-1}$

Then the process is

1) Spontaneous 2) Non spontaneous

3) At equilibrium

4) Can'be predicted from the information

9. At the vicinity of absolute zero

1) Cp – Cv 0 2) Cp Cv

3) Both 1 and 2 4) Cp > Cv

10. Correct relation among the following

1) $\Delta G_{system} = -\Delta S_{total}$

2) $\Delta G_{system} = -T\Delta S_{total}$

3) $\Delta G = \Delta H + T\Delta S$ 4)

11. A reaction occurs spontaneously when

(1) $\Delta G$ is +ve

(2) is –ve and is +ve

(3) is +ve and is –ve

(4) Both are +ve and

12. The mixing of gases is generally accompanied by

(1) Decrease in entropy

(2) Decrease in free energy

(3) Change in heat content

(4) Increase in free energy

13. For a spontaneous process, the change in Gibbs function is equal to the

(1) Heat content of the system

(2) Entropy change of the system

(3) Work of expansion

(4) Useful work

14. For the precipitation reaction of $Ag^+$ ions with NaCl, which is true?

(1) (2)

(3) (4)

15. The value of for the process $H_2O(s)$ $H_2O(l)$ at 1 atm and 260 K is

(1) < 0 (2) = 0

(3) > 0 (4) Unpredictable

16. For a reaction to occur spontaneously

(1) must be negative

(2) must be negative

(3) must be negative

(4) must be negative

17. Which of the following relation is incorrect?

(1) (2)

(3) $-\Delta G = -W_{non.exp}$ (4)

## KEY

| | | | |
|---|---|---|---|
| 1) 3 | 2) 4 | 3) 4 | 4) 4 |
| 5) 1 | 6) 1 | 7) 1 | 8) 1 |
| 9) 3 | 10) 2 | 11) 2 | 12) 2 |
| 13) 4 | 14) 3 | 15) 3 | 16) 1 |
| 17) 1 | | | |

## LEVEL - II

1. Combustion of hydrogen in a fuel cell at 300 K is represented as $2H_2(g) + O_2(g)$ $2H_2O(g)$. If and are –241.60 KJ $mol^{-1}$ and –228.40 KJ $mol^{-1}$ of $H_2O$. The value of for the above process is

(1) 4.4 kJ (2) –88 J

(3) +88 J (4) –44 J

2. In certain chemical reaction = 150 kJ and is 100 $JK^{-1}$ at 300 K. The value of would be

(1) Zero (2) 300 kJ

(3) 330 kJ (4) 120 kJ

3. The standard free energy change for a gaseous reaction at 27°C is X kCal. If equilibrium constant for a reaction is 100 and R is 2 cal $K^{-1}mol^{-1}$. Then X is

(1) –2.7636 (2) –2.6736

(3) +2.6736 (4) +2.7636

4. The standard free energy for formation of HI(g) is +1.7 kJ $mol^{-1}$. The value of equilibrium constant for the reaction $H_2(g) + I_2(g)$ 2HI(g) is the antilog of

(1) –114.18 (2) 114.18

(3) $-1.37 \times 10^{-3}$ (4) $1.37 \times 10^{-3}$

5. If of pure water at 100°C is 40.627 kJ $mol^{-1}$. The value of is

(1) 108.91 kJ $mol^{-1}$ (2) 108.91 $JK^{-1}mol^{-1}$

(3) 606.27 $JK^{-1}mol^{-1}$ (4) 808.27 $JK^{-1}mol^{-1}$

6. A system absorbs 20 KJ of heat and also does 10KJ of work. The net internal energy of the system

1) Increases by 10 KJ 2) Decreases by 10 KJ

3) Increases by 30 KJ 4) Decreases by 30 KJ

7. One mole of ideal gas expands freely at 310 K from five litre volume to 10 litre volume. Then and of the process are respectively

(1) 0 and 5 cal (2) 0 and 5 × 300 cal

(3) 0 and 0 (4) 5 and 0 cal

8. If a gas absorbs 200 J of heat and expands by 500 $cm^3$ against a constant pressure of $2 \times 10^5\ Nm^{-2}$, then change in internal energy is

(1) –300 J (2) –100 J

(3) +100 J (4) +300 J

9. A system absorbs 10 kJ of heat and does 4 kJ of work. The internal energy of the system

(1) Decreases by 6 kJ (2) Increases by 6 kJ

(3) Decreases by 14 kJ(4) Decreases by 14 kJ

### KEY

1) 2  2) 4  3) 1  4) 1
5) 2  6) 1  7) 3  8) 3
9) 2

## LEVEL - III

1. When enthalpy and entropy change for a chemical reaction are $-2.5\times10^{3}$ cals and 7.4 cals deg$^{-1}$ respectively. Predict that reaction at 298 K is
   1) spontaneous  2) reversible
   3) irreversible  4) non-spontaneous
2. The value ΔS for the process

   at 1 atm pressure and 260K is greater than zero. The value of ΔG will be
   1) > 0  2) < 0
   3) = 0  4) lies between – 1 and 0
3. At $0^{0}$C ice and water are in equilibrium. If ΔH for the process $H_2O(s)\longrightarrow H_2O(l)$ is 6.0 kJ mol$^{-1}$. The value of ΔS for conversion of water to ice in JK$^{-1}$ mol$^{-1}$ is
   1) 21.97  2) – 21.97
   3) 6.0  4) – 6.30
4. If $\Delta H_{\text{lattice}}$ and $\Delta H_{\text{hydration}}$ of NaC$l$ are respectively 778 and – 774.3 kJmol$^{-1}$ and $\Delta S_{\text{dissolution}}$ of NaC$l$ at 298K = 43 J mol$^{-1}$. The value of $\Delta G^{0}$ for dissociation of 1 mole of NaC$l$ is
   1) – 9.114 kJ  2) – 11.14 kJ
   3) –7.114 kJ  4) + 9.114 kJ
5. When a certain amount of ethylene was combusted, 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of $O_2$ (at NTP) that entered into the reaction is :
   1) 296.5 mL  2) 296.5 litre
   3) 6226 × 22.4 litre  4) 22.4 litre
6. The heats of neutralisation of four acids A, B, C, D are – 13.7, –9.4, – 11.2 and –12.4 kcal respectively when they are neutralised by a common base. The acidic character obeys the order :
   1) A > B > C > D  2) A > D > C > B
   3) D > C > B > A  4) D > B > C > A
7. Under the same conditions how many mL of 1 M KOH and 0.5 M $H_2SO_4$ solutions, respectively when mixed for a total volume of 100 mL produce the highest rise in temperature
   1) 67 : 33  2) 33 : 67  3) 40 : 60  4) 50 : 50
8. Given $\Delta_{\text{ioniz}}H°(\text{HCN}) = 45.2$ kJ mol$^{-1}$ and kJ mol$^{-1}$. Which one of the following facts is true ?
   1) $pK_a(HCN) = pK_a(CH_3COOH)$
   2) $pK_a(HCN) > pK_a(CH_3COOH)$
   3) $pK_a(HCN) < pK_a(CH_3COOH)$
   4) $pK_a(HCN) = (45.17/2.07)\ pK_a(CH_3COOH)$
9. The molar enthalpies of combustion of $C_2H_2$ (g), C(graphite) and $H_2$(g) are – 1300, – 394 and – 286 kJ mol$^{-1}$. respectively. The standard enthalpy of formation of $C_2H_2$(g) is
   1) – 226 kJ mol$^{-1}$  2) – 626 kJ mol$^{-1}$
   3) 226 kJ mol$^{-1}$  4) 626 kJ mol$^{-1}$

### KEY

1) 1  2) 1  3) 2  4) 1  5) 2
6) 2  7) 4  8) 2  9) 4

## PREVIOUS AIEEE QUESTIONS

### 2007

1. In conversion of lime - stone to lime,

   then values of $\Delta H^{0}$ are + 179. 1 KJ and 160. 2 J/K
   [illegible] respectively at 298 K and 1 bar. Assuming that and do not change with temperature, temperature above which conversion of lime-stone to lime will be spontaneous is
   1) 1118 K  2) 1008 K
   3) 1200 K  4) 845 K

Key : 1

2. Assuming that water vapour is an ideal gas, the internal energy change ( ) when 1 mol of water is vapourised at 1 bar pressure and 100 , ( Given : Molar enthalpy of vaporisation of water at 1 bar and 373 K = 41 kJ and R = 8.3 J ) will be
   1) 41. 00 kJ  2) 4.100 kJ
   3) 3. 7904 kJ  4) 37. 904

Key : 4

3. Identify the correct statement regarding a spontaneous process :
   1) Lowering of energy in the reaction process is the only crioterion for spontaneity
   2) For a spontaneous process in a isolated system, the change in entropy is positive
   3) Endothermic processes are never spontaneous
   4) Exothermic processes are always spontaneous

Key : 2