**1.9Statement of Third Law of Thermodynamics:**

The third law of thermodynamics states that the entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.

Entropy, ‘S’, is a measure of the disorder/randomness in a closed system. It is directly related to the number of a fixed microscopic state that can be occupied by a system and accessible by the system, the greater its entropy.

Mathematically,  
**LimT –>0S = 0**

If the entropy is zero at temperature T = o, then this law states that the absolute entropy Sab of a substance at temperature T and pressure P.

## 1.9.1The Third Law -Calculate Absolute Entropies

Theabsolute entropyof a substance at any temperature above 0 K must be determined by calculating the increments of heatqrequired to bring the substance from 0 K to the temperature of interest, and then summing the ratiosq/T.

Two kinds of experimental measurements are needed:

**1.**The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to theheats of fusionandvaporization. The entropy increase associated with transition at temperatureTisΔHfusion / T

**2**. Theheat capacityCof a phase expresses the quantity of heat required to change the temperature by a small amountΔT, or more precisely, by an infinitesimal amountdT.Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantitiesCPdTfor each increment of temperature T. This is of course just the integral

S0→T=∫T0CpTdt

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence ofCp onTbe used in the integral in equation.

**Multiple Choice Questions-**

**1.** Which one of the following definitions best describes the concept of work?

1. the flow of energy from one object or substance to another due to a difference in temperature
2. the flow of energy from one body to another through uniform molecular motion
3. the force associated with molecular motion
4. he random motion of molecules in a gas at low pressure

**2.**An isolated system is best described by which one of the following

Statements?

(a) Neither matter nor heat can pass into or out of the system

(b) The system has a boundary which allows heat to be transferred but does not allow material to pass into or out of the system

(c) The system has a diathermic boundary

(d) A system which has reached thermal equilibrium with its surroundings

**3.** Which one of the following statements describes a path function?

(a) A property of a system that depends only on the current state ofthe system, not on the path the system took to reach that state

(b) A property of a system that depends on the path taken between theinitial and final states

(c) The sum of kinetic and potential energy contained in a substance

(d) The heat energy absorbed by a system at constant pressure

**4.** Consider the following thermodynamic properties.

i) Work done on a system

ii) Heat absorbed

iii) Entropy

iv) Enthalpy

Which of these properties are state functions?

(a) i) and ii) only

(b) i) and iii) only

(c) i)only

(d) iii) and iv) only

**5.**Which of the following statements best describes the Second Law of Thermodynamics?

(a) The internal energy of the universe is constant

(b) Energy can be neither created nor destroyed.

(c) When an isolated system undergoes a spontaneous change, the entropy of

the system will increase.

(d) At absolute zero, the entropy of a perfect crystal is considered to be zero.

**6.** Which of the following statements will always apply when a reversible

Chemical reaction has attained equilibrium?

1. All reactants will convert to products
2. The reaction proceeds alternately in the forward and reverse directions
3. The Gibbs free energy of the system reaches a minimum
4. The forward reaction will dominate over the reverse reaction

**7.the extensive properties of a system, \_\_\_\_\_\_\_**

1. are independent of the mass of the system
2. depend upon temperature of the system

(c) Depend upon the mass of the system

(d) None of the above

**8.**The variations in enthalpy that cannot be detected per calorimeter can be detected with the aid of

(a) Newton’s law (b) Hess’s law (C) Krebs law (d) Ohm’s law

**9.**The energy required to sever a given covalent bond is named

(a)Bond energy (b) bond enthalpy (c) bond dissociation energy (d) all of above

**10.** Changes in enthalpy in an exothermic reaction is

(a)Positive (b) negative (c) constant (d) neutral

**11.**The first law of thermodynamics states that energy cannot be

(a) Createdonly (b) destroyed only (c) converted (d) created and destroyed

**12.**The change in the energy between a chemical reaction and the surroundings at constant temperature is called

1. enthalpy change (b) enthalpy (c) enthalpy profile(d) dynamic enthalpy

**13**. To initiate a reaction the minimum energy which is required to break bonds is called

(a) Bond energy (b) activation energy(c) breaking energy (d) ionization energy

**14.** Energy has different forms which include

(a) Heat (b) work(c) all of the mentioned (d) none of the mentioned

**15.**Which of the following represents the energy in storage?

(a) Heat (b) work(c) internal energy (d) none of the mentioned

**16.**By first law of thermodynamics,

(a) Q=ΔE-W(b) Q=ΔE+W (c) Q=-ΔE-W (d) Q=-ΔE+W

**17.** Which Thermodynamic process where heat is not exchanged with the surroundings is?

1. Isothermal(b) Adiabatic (c) Isobaric (d) Isotropic

**18.** What will be the value of ΔH, if the forward and reverse reactions have the same energy of activation?

(a) ΔH = ΔG = ΔS = 0(b) ΔS = 0(c) ΔG = 0(d) ΔH = 0

**19.**Which is true for the entropy of a spontaneous reaction?

(a) ΔS(system) – ΔS(surroundings) > 0(b) ΔS(system) + ΔS(surroundings) > 0

(c) ΔS(surroundings) > 0 only(d) ΔS(system) > 0 only

**20.** For endothermic reactions, what is the heat of reaction?

(a) Positive (b) Negative (c) Zero (d) Cannot Say

**21.**Third law of thermodynamics provides a method to evaluate which property?

(a) Absolute Energy(b) Absolute Enthalpy(c) Absolute Entropy(d) Absolute Free Energy

**22.** The species which by definition has ZERO standard molar enthalpy of formation at 298 K is

(a) Br2(g) (b) Cl2(g) (c) H2O(g) (d) CH4(g)

**23.** Which of the following is true for the reaction? H2O (l) ↔ H2O (g) at 100° C and 1 atm pressure

(a) ∆S = 0(b) ∆H = T ∆S(c) ∆H = ∆U(d) ∆H = 0

**24.** In which of the following process, a maximum increase in entropy is observed?

(a) Dissolution of Salt in Water (b) Condensation of Water

(c) Sublimation of Naphthalene (d) Melting of Ice

**25.** The bond energy (in kcal mol-1) of a C-C single bond is approximately

(a) 1(b) 10(c) 83-85(d) 1000

**26.** Which thermodynamic function accounts automatically for enthalpy and entropy both?

(a) Helmholtz Free Energy (A)(b) Internal Energy (E)

(c) Work Function(d) Gibbs free energy

**27.** Which bond is most polar?

(a)N-F (b) C-O (c) O-F(d) C-F

**28.**What is correct about bond order?

(a) it always has an integral value

(b) it can have any value positive, integral or fraction including zero

(c) it can have any value greater than zero

(d) all the above statements are correct

**29.**The weak forces between molecules are called

(a)molecular forces(b) intermolecular forces

(c) intramolecular forces (d) extramolecular forces

**30.**Bond energy refers to the

(a)energy required to make a mole of a compound

(b)energy required to break a mole of a compound

(c)energy required to carry out sublimation

(d)none of the above

**31.**The energy which is required to break 1 mole of a given bond is called

(a)bond energy (b) molar energy (c) molar bond energy

1. bond breaking energy

**Answers—**

1. **(b) 2.(a)3.( b)4.(d)5. (c)6.(c)7.(c)8. ( b)9. (d)10.( b)**

**11. (d)12. (a)13. (a)14. (c)15.(c)16.( b)17.( b)18. (d)**

**19.( b)20.(a)21. (c)22.( b) 23. (a)24. (c) 25. (c) 26. (d)**

**27. (d)28. ( b)29.( b)30.( b)31.(a)**