UNIT-7 THERMODYNAMICS

MY REVISION TIMELINE:-

SUMMARY:-

- Universe
    - System
        - Homogeneous
        - Heterogeneous
    - Surrounding
- Boundary: Separates system from its surrounding
- Types of system:
    - Open
    - Close
    - Isolated
- Properties of system:
    - Extensive (depends on mass or size of the system)
    - Intensive (Independent of mass or size of the system)
- Types of processes
    - Reversible
    - Irreversible
    - Adiabatic ($q=0$)
    - Isothermal ($dT=0$)
    - Isobaric ($dP=0$)
    - Isochoric ($dV=0$)
    - Cyclic ($dU=0$, $dH=0$, $dP=0$, $dV=0$, $dT=0$)
- State function: Thermodynamic property of a system, which has a specific value for a given state and does not depend on the path or manner by which the particular state is reached.
- Path function: Thermodynamic property of the system whose value depends on the path by which the system changes from its initial state to final state.
- Internal energy (U): Internal energy of a system is equal to the energy possessed by all its constituents (atoms, ions and molecules)

  $U = U_t + U_v + U_x + U_b + U_e + U_i$
- Heat (q):
    - SI Unit is Joule (J)
    - Heat flow into the system (+q)
    - Heat flow out of the system (-q)

- Work (w):
  - SI Unit is Joule (J)
  - -w = F.x
  - (-) sign indicates that work has to done by the system
- $w_{rev} = -2.303\ nRT\ \log(\frac{V_f}{V_i})$
- Zeroth law of thermodynamics: If two systems are separately in thermal equilibrium with a third one then they tend to be in thermal equilibrium with themselves.
- First law of thermodynamics: The total energy of an isolated system remains constant though it may change from one form to another.
  $\Delta U = q+w$
- $H = U + PV$
- $\Delta H = q_p$
- $\Delta H = \Delta U + \Delta n_{(g)}RT$
- Standard heat of formation: The change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states.
- Heat of combustion: The change in enthalpy of a system when one mole of a substance is completely burnt in excess of air or oxygen.
- The amount of heat absorbed by one mole of a substance to raise its temperature by 1 Kelvin.
- $C_p - C_v = nR$
- $\Delta H = nC_p\ (T_2 - T_1)$
- $\Delta H_C{}^{\circ}{}_{(pressure)} = \Delta U_C{}^{\circ}{}_{(vol)} + \Delta n_g RT$
- $q = m_w C_w \Delta T$
- Heat of solution: The change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.
- Heat of neutralisation: The change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution.
- Molar heat of fusion: The change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point.
- Molar heat of vaporisation: The change in enthalpy when one mole of liquid is converted into vapour state at its boiling point.
- Molar heat of sublimation: The change in enthalpy when one mole of a solid is directly converted into the vapour state at its sublimated temperature.
- Heat of transition: The change in enthalpy when one mole of an element changes from one of its allotropic form to another.
- Hess's law: The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.
- Lattice energy ($\Delta H_{lattice}$): Amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance.
- Various statements of second law of thermodynamics:

- Entropy statement: The entropy of an isolated system increases during a spontaneous process.
- Kelvin-Planck statement: It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink
- Clausius statement: It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

- SI unit of entropy: JK^{-1}
- Standard entropy change ($\Delta S°$) = $\Sigma S°_{products} - \Sigma S°_{reactants}$
- $\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{rev}}{T}$
- Entropy of fusion: The heat absorbed, when one mole of a solid melts at its melting point reversibly.
  $$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_F}$$
- Entropy of vapourisation: The heat absorbed, when one mole of liquid is boiled at its boiling point reversibly.
  $$\Delta S_V = \frac{\Delta H_V}{T_b}$$
- Entropy of transition: The heat change, when one mole of a solid changes reversibly from one allotropic to form another at its transition temperature.
  $$\Delta S_t = \frac{\Delta H_t}{T_t}$$
- Gibb's free energy (G) is the available energy to do work in a system.
  $G = H – TS$
  $\Delta G = \Delta H - T\Delta S$
- For spontaneous reaction $\Delta G < 0$ (i.e.) $\Delta H - T\Delta S < 0$
- $-\Delta G = W + P\Delta V$
- $\Delta G = \Delta G° + RT \ln Q$
- Third law of thermodynamics: The entropy of pure crystalline substance at absolute zero is zero (or) It is impossible to lower the temperature of an object to absolute zero in a finite number of steps. $\lim_{T\to 0} s = 0$ for a perfectly ordered crystalline state.

FORMULAS:-

- $C_v = (\frac{\delta V}{\delta T})_v$
- $C_p = (\frac{\delta H}{\delta T})_p$
- $C_p – C_v = nR$
- $H = U + P\Delta V$ or $\Delta H = \Delta U + P\Delta V$
- $\Delta H = \Delta U + RT\Delta ng$
- $ds = \frac{d_{q_{rev}}}{T}$
- % Efficiency = $\%\eta = (1 - \frac{T_c}{T_h}) \times 100$

- $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T}$
- $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$
- $\Delta G = W + P\Delta V$ or $-\Delta G = -W - P\Delta V$
- $\Delta G = \Delta G^\circ + RT \ln Q$
- Vant Hoff's equation: $\Delta G^\circ = -RT \ln K_{eq}$

TEXTBOOK EVALUATION

Multiple choice questions:-

1. The amount of heat exchanged with the surrounding at constant temperature and pressure is called

(a) ΔE **(b) ΔH**
(c) ΔS (d) ΔG

2. All the naturally occurring processes proceed spontaneously in a direction which leads to

(a) decrease in entropy (b) increase in enthalpy
(c) increase in free energy **(d) decrease in free energy**

3. In an adiabatic process, which of the following is true?

(a) $q = w$ **(b) $q = 0$**
(c) $\Delta E = q$ (d) $P\Delta V = 0$

4. In a reversible process, the change in entropy of the universe is

(a) >0 (b) > 0
(c) < 0 **(d) $= 0$**

5. In an adiabatic expansion of an ideal gas

(a) $w = -\Delta u$ (b) $w = \Delta u + \Delta H$
(c) $\Delta u = 0$ (d) $w = 0$

6. The intensive property among the quantities below is

(a) mass (b) volume
(c) enthalpy **(d) mass/volume**

7. An ideal gas expands from the volume of 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300K against a constant pressure at 1×10^5 Nm^{-2}. The work done is

(a) – 900 J (b) 900 kJ
(c) 270 kJ (d) – 900 kJ

Explanaton:

$P = 1 \times 10^5$ Nm^{-2}
$\Delta v = 1 \times 10^{-2} - 1 \times 10^{-3} = 9 \times 10^{-3}$
$w = -P\Delta V$
$w = -9 \times 10^2$ J

$$\boxed{w = -900\ J}$$

8. Heat of combustion is always

(a) positive **(b) negative**
(c) zero (d) either positive or negative

9. The heat of formation of CO and CO_2 are -26.4 kcal and -94 kcal, respectively. Heat of combustion of carbon monoxide will be

(a) +26.4 kcal **(b) -67.6 kcal**
(c) -120.6 kcal (d) +52.8 kcal

Explanation:

$CO_{(g)} + O_{2(g)} \rightarrow CO_{2(g)}$

ΔH_C^o (CO) = $[\Delta H_f(CO_2) – \Delta H_f(CO) + \Delta H_f(O_2)]$

ΔH_C^o (CO) = -94 KCal – [- 26.4 KCal + 0]

ΔH_C^o (CO) = -94 KCal + 26.4 Kcal

$\boxed{\Delta H_C^o \text{ (CO)} = -67.4 \text{ KCal}}$

10. C(diamond) → C(graphite), ΔH = -ve, this indicates that

(a) graphite is more stable than diamond
(b) graphite has more energy than diamond
(c) both are equally stable
(d) stability cannot be predicted

11. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ, respectively. ΔH for reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is

(a) -1365 kJ (b) 2730 kJ
(c) -2730 kJ **(d) -462 kJ**

Explanation:

$2A1 + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$

$\Delta H_r^o = [2\ \Delta H_f\ (Cr) + \Delta H_f\ (Al_2O_3)] – [2\ \Delta H_f\ (Al) + \Delta H_f\ (Cr_2O_2)]$

$\Delta H_r^o = [0 + (-\ 1596\ kJ)] – [0 + (-\ 1134)]$

$\Delta H_r^o = –\ 1596\ kJ + 1134\ kJ$

$\boxed{\Delta H_r^o = –\ 462\ kJ}$

12. Which of the following is not a thermodynamic function?

(a) internal energy (b) enthalpy
(c) entropy **(d) frictional energy**

13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then

(a) $\Delta H > \Delta U$ (b) $\Delta H – \Delta U = 0$
(c) $\Delta H + \Delta U = 0$ **(d) $\Delta H < \Delta U$**

14. Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is

(a) +1 kJ (b) -5 kJ
(c) +3 kJ (d) -3 kJ

Explanation:

$\Delta U = q + w$

$\Delta U = -1kJ + 4kJ$

$\boxed{\Delta U = +3kJ}$

15. The work done by the liberated gas when 55.85 g of iron (molar mass 55.85 g mol^{-1}) reacts with hydrochloric acid in an open beaker at 25°C

(a) -2.48 kJ (b) -2.22 kJ
(c) +2.22 kJ (d) + 2.48 kJ

Explanation:

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

$\therefore n = 1$

$T = 25°C = 298\ K$

$w = -P(\frac{nRT}{P})$

$w = -nRT$

$w = -1 \times 8314 \times 298\ J$

$w = 2477.57\ J$

$\boxed{\boldsymbol{w = -2.48\ k\ J}}$

16. The value of AH for cooling 2 moles of an ideal mono atomic gas from 125°C to 25°C at constant pressure will be [given $C_P = 5/2\ R$]

(a) -250 R **(b) -500 R**

(c) 500 R (d) +250 R

Explanation:

$\Delta H = nC_p\ (T_f - T_i)$

$\Delta H = 2 \times \frac{5}{2} R\ (298 - 398)$

$\boxed{\boldsymbol{\Delta H = -500\ R}}$

17. Given that $C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H° = a$ kJ; $2\ CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ $\Delta H° = -b$ kJ; Calculate the ΔH° for the reaction $C_{(g)} + H_2O_{2(g)} \rightarrow CO_{(g)}$

(a) $\frac{b+2a}{2}$ (b) 2a – b

(c) $\frac{2a-b}{2}$ **(d) $\frac{b-2a}{2}$**

Explanation:

$C + O_2 \rightarrow CO_2$ $\Delta H° = -a$ kJ → (1)

$2CO + O_2 \rightarrow 2CO_2$ $\Delta H° = -b$ kJ → (2)

$C + ½O_2 \rightarrow CO$ $\Delta H° = ?$

(1) x (2)

$2C + 2O_2 \rightarrow 2CO_2$ $\Delta H° = -2a$ kJ → (3)

Reverse of equestion (2) will be

$2CO_2 \rightarrow 2CO + O_2$ $\Delta H° = +b$ kJ → (4)

(3) + (4)

$2C + O_2 \rightarrow 2CO$ $\Delta H° = b - 2a$ kJ → (5)

(5) ÷ (2)

$\boxed{\boldsymbol{C + O_2 \rightarrow CO\ \Delta H° = \frac{b-2a}{2}\ kJ}}$

18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at 0°C and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat released from this combustion in kJ is ($\Delta H_C\ (CH_4) = -890$ kJ mol^{-1} and $\Delta H_C\ (C_3H_8) = -2220$ kJ mol^{-1})

(a) -889 kJ (b) -1390 kJ

(c) -3180 kJ **(d) -653.66 kJ**

Explanation:

Let the mixture contain x litre of methane and (15.68 -x) litre of propane.

CH_4 (x) + $2O_2$ (2x) → CO_2 +$2H_2O$

C_3H_8 (15.68-x) + $5O_2$ [5(15.68-x)] → $3CO_2$ + $4H_2O$

Volume of oxygen consumed = 2x + 5 (15.68-x) = 32 litre

x = 15.47 litre

$$\Delta H_C = \left[\frac{\Delta H_C(CH_4)}{22.4\ \text{lit}}\times(x)\ \text{lit}\right] + \left[\frac{\Delta H_C(C_2H_4)}{22.4\ \text{lit}}\times(3.67-x)\ \text{lit}\right]$$

$$\Delta H_C = \left[\frac{-890\ \text{kJ mol}^{-1}}{22.4\ \text{lit}}\times 1.23\ \text{lit}\right] + \left[\frac{-1423}{22.4\ \text{lit}}\times(3.67-1.23)\ \text{lit}\right]$$

ΔH_C = [- 614.66 kJ mol^{-1}] + [- 20.81 kJ mol^{-1}]

$$\boxed{\Delta H_C = -635.47\ kJ\ mol^{-1}}$$

19. The bond dissociation energy of methane and ethane are 360 kJ mol^{-1} and 620 Id mol^{-1} respectively. Then, the bond dissociation energy of C-C bond is

(a) 170 kJ mol^{-1} (b) 50 kJ mol^{-1}

(c) 80 kJ mol^{-1} (d) 220 kJ mol^{-1}

Explanation:

$4E_{C-H}$ = 360 kJ mol^{-1}

E_{C-H} = 90 kJ mol^{-1}

E_{C-C} + $6E_{C-H}$ = 620 KJ mol^{-1}

E_{C-C} + 6 x 90 = 620 kJ mol^{-1}

E_{C-C} + 540 = 620 kJ mol^{-1}

$$\boxed{E_{C-C} = 80\ kJ\ mol^{-1}}$$

20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET phase – I)

(a) $\Delta H<0$ and $\Delta S>0$ (b) $\Delta H<0$ and $\Delta S<0$

(c) $\Delta S>0$ and $\Delta S = 0$ (d) $\Delta H<0$ and $\Delta S>0$

21. The temperature of the system, decreases in an

(a) isothermal expansion (b) isothermal compression

(c) adiabatic expansion (d) adiabatic compression

22. In an isothermal reversible compression of an ideal gas the sign of q, AS and w are respectively

(a) +, -, – (b) -, +, –

(c) +, -, + **(d) -, -, +**

Explanation:

During compression q = -ve. So entropy decreases and work is done on the system (i.e.) w = -ve

23. Molar heat of vaporization of a liquid is 4.8 kJ mol^{-1}. If the entropy change is 16 J mol^{-1} K^{-1}. the boiling point of the liquid is

(a) 323 K **(b) 27°C**

(c) 164 K (d) 0.3 K

Explanation:

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$T_b = \frac{4800}{16}$$

$$\boxed{\mathbf{T_b = 300\ K = 27°C}}$$

24. ΔS is expected to be maximum for the reaction

(a) $Ca_{(S)} + O_{2(g)} \rightarrow CaO_{(S)}$

(b) $C_{(S)} + O_{2(g)} \rightarrow CO2_{(g)}$

(c) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$

(d) $CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)}$

Explanation:

In $CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)}$ gaseous product is given by solid reactant hence ΔS is maximum for this reaction.

25. The values of H and S for a reaction are respectively 30 kJ mol^{-1} and loo kJ mol^{-1}. Then the temperature above which the reaction will become spontaneous is

(a) 300 K

(b) 30 K

(c) 100 K

(d) 20°C

Explanation:

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

At 300 K,

$\Delta G = 30000\ J\ mol^{-1} - 300\ K \times 100\ JK\ mol^{-1}$

$\Delta G = 0$

Above **300 K**, ΔG will be negative and reaction becomes spontaneous.

Write brief answers to the following questions:-

26. State the first law of thermodynamics.

The **total energy** of an **isolated system remains constant** though it may change from **one form to another**.

$\mathbf{\Delta U = q + w}$

where ΔU = change in internal energy
q = heat supplied to the system
w = work done on the system

27. Define Hess's law of constant heat summation.

The **enthalpy change of a reaction** either at **constant volume** or **constant pressure** is the same whether it takes place in a single or multiple steps provided the **initial** and **final states are same**.

$$\begin{tikzcd}
A \arrow[rrr, "\Delta H_f"] \arrow[dr, "\Delta H_1"] & & & B \\
& X \arrow[r, "\Delta H_2"] & Y \arrow[ur, "\Delta H_3"] &
\end{tikzcd}$$

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3$$

28. Explain intensive properties with two examples.

- The property that is **independent of the mass or the size of the system** is called an intensive property.
- **Example**: Density, temperature etc…

29. Define the following terms:
a. isothermal process b. adiabatic process
c. isobaric process d. isochoric process

- **Isothermal process:**
  - It is defined as one in which the **temperature of the system remains constant**, during the change **from its initial to final states**.
  - dT = 0
- **Adiabatic process:**
  - It is defined as one in which there is **no exchange of heat** (q) between the **system** and **surrounding** during operations.
  - q = 0
- **Isobaric process:**
  - It is defined as one in which the **pressure of the system remains constant** during its change **from its initial to final state**.
  - dP = 0
- **Isochoric process:**
  - It is defined as one in which the **volume of system remains constant** during its change **from its initial to final state** of the process.
  - dV = 0

30. What is the usual definition of entropy? What is the unit of entropy?

- Entropy is a measure of the **molecular disorder or randomness** of a system.
- **ds =** $\frac{d_{q_{rev}}}{T}$
- Unit: **JK^{-1}**

31. Predict the feasibility of a reaction when
i) both ΔH and ΔS positive ii) both ΔH and ΔS negative
iii) ΔH decreases but ΔS increases

- **Both ΔH and ΔS positive:**
  - At low T: Non spontaneous and non-feasible.
  - At high T: Spontaneous and feasible.
- **Both ΔH and ΔS negative**
  - At low T: Spontaneous and feasible.
  - At high T: Non spontaneous and non-feasible.
- **ΔH decreases but ΔS increases**
  - Spontaneous at all T and feasible.

32. Define Gibb's free energy.

- Gibb's free energy is the **available energy to do work** in a system
- **G = H-TS**

33. Define enthalpy of combustion.

The **change in enthalpy** of a system when **one mole** of the substance is **completely burnt** in excess of air or oxygen.

34. Define molar heat capacity. Give its unit.

- The amount of **heat absorbed** by **one mole** of a substance to **raise** its **temperature** by **1 Kelvin**.
- Unit: **$JK^{-1}mol^{-1}$**

35. Define the calorific value of food. What is the unit of calorific value?

- Amount of **heat produced** in **calories** or **joules** when **one gram** of the substance is **completely burnt.**
- Unit: **Jkg^{-1} or $Calg^{-1}$**

36. Define enthalpy of neutralization.

The **change in enthalpy** when **one gram equivalent of an acid** is completely neutralised by **one gram equivalent of a base** or vice versa in **dilute solution**.

37. What is lattice energy?

The **amount of energy** required to completely **remove the constituent ions** from its **crystal lattice** to an **infinite distance**.

38. What are state and path functions? Give two examples.

- A state function is a **thermodynamic property** of a system, which has a **specific value** for a given state and does **not depend on the path** by which the particular state is reached. **Example:** Pressure (P), Volume (V), Temperature (T), Free energy (G) etc…
- A path function is a **thermodynamic property** of a system whose **value depends on the path** by which the system changes from its initial to final states. **Example:** Work (w), Heat (q) **Work** will have **different values** if the process is carried out **reversibly or irreversibly.**

39. Give Kelvin statement of second law of thermodynamics.

It is **impossible to construct a machine** that **absorbs heat** from a **hot source** and converts it completely into **work** by cyclic process **without transferring a part of heat** to a cold sink.

40. The equilibrium constant of a reaction is 10, what will be the sign of ∆G? Will this reaction be spontaneous?

$\Delta G° = -2.303\ RT \log K_{eq}$

$K_{eq} = 10$

$\therefore \Delta G°$ = -ve value.

So the reaction will be **spontaneous**.

41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

It is based on **Arrhenius theory of acids and bases** according to which strong acids and strong bases **completely ionise** in **aqueous solution** to produce H^+ and OH^- ions respectively.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \quad \Delta H = -57.32\ kJ$$

42. State the third law of thermodynamics.

- The entropy of a **pure crystalline substance** at absolute zero is **zero**.
- It is impossible to lower the temperature of an object to absolute zero in a **finite number of steps.**

43. Write down the Born-Haber cycle for the formation of $CaCl_2$.

Born – Haber cycle for the formation of $CaCl_2$:

$Ca_{(S)} + Cl_{2(l)} \rightarrow CaC_{2(S)}$ $\Delta H_f°$
Sublimation : $Ca_{(S)} \rightarrow Ca_{(S)}$ $\Delta H_1°$
Ionization : $Ca_{(g)} \rightarrow Ca^{2+}_{(g)} + 2e^{-} = \Delta H_2°$
Vapourisation : $Cl_{2(l)} \rightarrow Cl_{2(g)} = \Delta H_3°$
Dissociation : $Cl_{2(g)} \rightarrow 2Cl_{(g)} = \Delta H_4°$
Electron affinity : $2Cl_{2(g)} + 2e^{-} \rightarrow 2Cl^{-2}_{(g)} = \Delta H_5°$
Lattice enthalpy : $Ca^{2+}_{(g)} + 2Cl^{-}_{(g)} \rightarrow CaCl_{2(S)} = \Delta H_6°$
$\mathbf{\Delta H_f° = \Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4° + \Delta H_5° + \Delta H_6°}$

44. Identify the state and path functions out of the following: a)Enthalpy b)Entropy c) Heat d) Temperature e) Work f) Free energy.

- **State functions:**
  - Enthalpy
  - Entropy
  - Temperature
  - Free energy
- **Path functions:**
  - Heat
  - Work

45. State the various statements of second law of thermodynamics.

- **Entropy statement:**
  The entropy of an **isolated system increases** during a spontaneous process.
- **Kelvin-Planck statement:**
  It is **impossible to construct a machine** that **absorbs heat** from a **hot source** and converts it completely into **work** by cyclic process **without transferring a part of heat** to a cold sink.

  $$\boldsymbol{\eta = \left(1 - \frac{|q_c|}{|q_h|}\right)}$$
- **Clausius statement:**
  It is impossible to **transfer heat from a cold reservoir to a hot reservoir without doing some work**.
- **Efficient statement:**
  Even an **ideal, frictionless engine** cannot correct 100% of its input heat into work.

  $$\textbf{\% Efficiency} = \left(1 - \frac{T_c}{T_h}\right) \times 100$$

  Where
  T_c = Temperature of the cold reservoir (sink)
  T_h = Temperature of the hot reservoir (source)

46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?

A reaction that occurs under the **given set of conditions without any external driving force** is called spontaneous reaction.

Conditions for spontaneity of a process:

- If **enthalpy change of a process is negative**, then the process is **exothermic** and occurs spontaneously. Therefore **ΔH should be negative**.
- If **entropy change of a process is positive**, then the process occurs spontaneously, therefore **ΔS should be positive**.
- The **Gibb's free energy** which is the combination of the above two ($\Delta H = T\Delta S$) should be **negative** for a reaction to occur spontaneously, i.e. the necessary condition to be spontaneous is $\mathbf{\Delta H - T\Delta S < 0}$.

47. List the characteristics of internal energy.

- Internal energy of a system is an **extensive property.** It depends on the amount of substances present in the system. If the amount is doubles, theinternal energy is also doubled.
- Internal energy of a system is a **state function**. It depends only upon the state variables (T, P, V, n) of the system. The change in internal energy does not depend on the path by which the final state is reached.
- The change in internal energy of a system is expressed as $\mathbf{\Delta U = U_f - U_i}$
- In a **cyclic process**, there is no energy change $\mathbf{\Delta U_{(cyclic)} = 0}$.
- If the internal energy of the system at final state (Uf) is **less** than the internal energy of the system at its initial state (Ui), then ΔU would be **negative**.

  $\mathbf{U_f < U_i \; \Delta U = U_f - U_i = -ve}$
- If the internal energy of the system at final state (Uf) is **greater** than the internal energy of the system at its initial state (Ui), then ΔU would be **positive**.

  $\mathbf{U_f > U_i \; \Delta U = U_f - U_i = +ve}$

48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.

- Calorimeter is used for **measuring the amount of heat change** in a **chemical or physical** change.
- A known amount of **combustible substance** is **burnt** in **oxygen in the bomb**. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The **change in temperature** is measured using a **Beckman thermometer**. Since the bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a **constant volume ($\mathbf{\Delta U_c^o}$).**
- The amount of heat produced in the reaction (ΔU_c^o) is equal to the sum of the heat abosrbed by the calorimeter and water. Heat absorbed by the calorimeter

  $\mathbf{q_1 = k.\Delta T}$

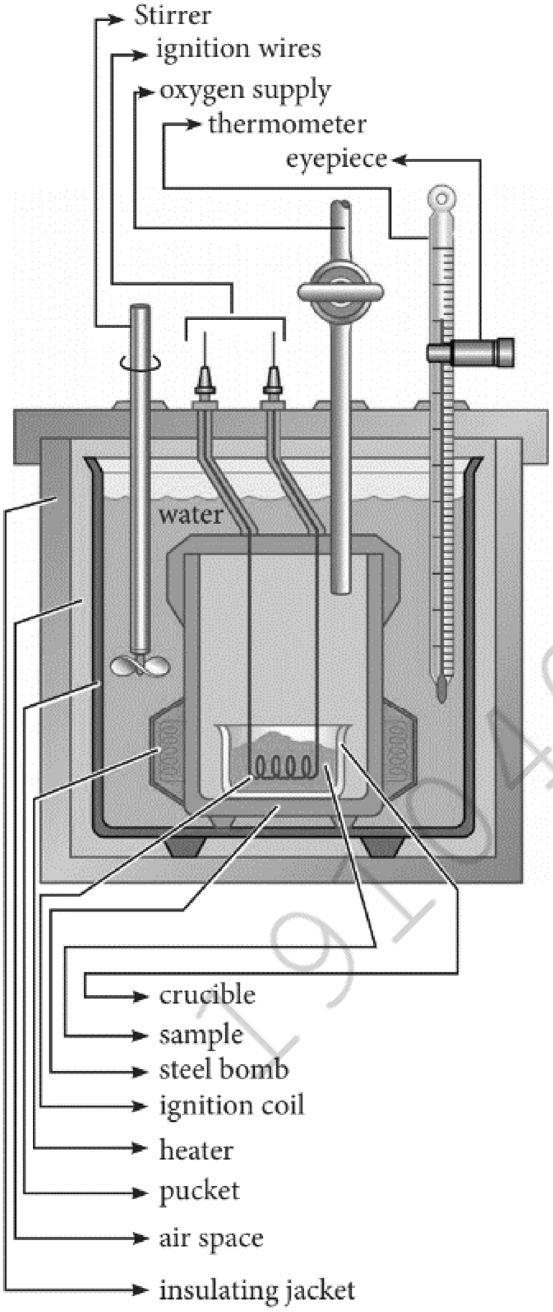
  where k is a calorimeter constant equal to $m_c C_c$ (m_c is mass of the calorimeter and C_c is heat capacity of calorimeter)
- Heat absorbed by the water

  $\mathbf{q_2 = m_w C_w \Delta T}$

  where m_w is molar mass of water

  C_w is molar heat capacity of water (75.29 J K^{-1} mol^{-1})
- Therefore $\Delta U_c = q_1 + q_2 = k.\Delta T + m_w C_w \Delta T = \mathbf{(k+m_w C_w)\Delta T}$

- Calorimeter constant can be determined by burning a known mass of standard sample (**benzoic acid**) for which the heat of combustion is known (-3227 $kJmol^{-1}$)
- The enthalpy of combustion at constant pressure of the substance is calculated from the equation $\mathbf{\Delta H_c^o{}_{(pressure)} = \Delta U_c^o{}_{(Vol)} + \Delta n_g RT}$



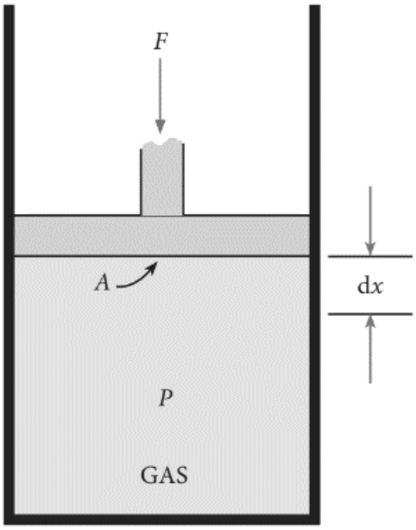
49. Calculate the work involved in expansion and compression process.

- The essential condition of expansion or compression of a system is, there should be **difference between external pressure** (P_{ext}) and **internal pressure** (P_{int}).
- Let us consider a cylinder which contains **'n' moles** of an ideal gas fitted with a **frictionless piston** of cross sectional **area A**. The total volume of the gas inside is $\mathbf{V_i}$ and pressure of the gas inside is $\mathbf{P_{int}}$.
- If the external pressure $\mathbf{P_{ext}}$ **is greater than** $\mathbf{P_{int}}$, the piston moves inward till the pressure inside becomes equal to P_{ext}. Let this change be achieved in a single step and the final volume be V_f.

- In this case, the **work is done on the system (+w).** It can be calculated as follows

  $\mathbf{w = -F . \Delta x} \rightarrow (1)$

  where dx is the distance moved by the piston during the compression and F is the force acting on the gas.



$\mathbf{F = P_{ext} A} \rightarrow (2)$

Substituting (2) in (1)

$w = -P_{ext}.A.\Delta x$

$A.\Delta x$ = change in volume = $V_f - V_i$

$w = -P_{ext}.(V_f - V_i)$

$w = -P_{ext}.(-\Delta V)$

$\mathbf{w = P_{ext}(\Delta V)}$

Since work is done on the system, it is a positive quantity.

- If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation.

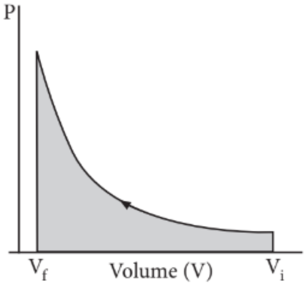
  $$\mathbf{w_{rev} = -\int_{V_i}^{V_f} P_{ext} dV}$$

- In a compression process, the external pressure is always greater than the pressure of the system.

  i.e $\mathbf{P_{ext} = (P_{int} + dP)}$

- In an expansion process, the external pressure is always less than the pressure of the system.

  i.e. $\mathbf{P_{ext} = (P_{int} - dP)}$



- When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from Vi to Vf, the **P-V plot** looks like in the graph. Work done on the gas is represented by the shaded area.

- $P_{ext} = (P_{int} + dP)$**.** Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$\mathbf{w_{rev}} = -\int_{V_i}^{V_f} P_{int} dV$$

- For a given system with an ideal gas,

$$P_{int} V = nRT$$

$$P_{int} = \frac{nRT}{V}$$

$$w_{rev} = -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$w_{rev} = -nRT \int_{V_i}^{V_f} \left(\frac{dV}{V}\right)$$

$$w_{rev} = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$w_{rev} = -2.303\ nRT \log\left(\frac{V_f}{V_i}\right)$$

- During **expansion**, work is done by the system, since $V_f > V_i$ the sign obtained for work will be **negative**.
- During **compression**, work is done on the system, since $V_f < V_i$ the sign obtained for work will be **positive**.

50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

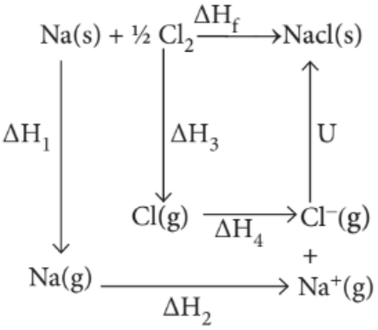
- When the system at constant pressure undergoes changes from an **initial state with H_1, U_1, V_1 and P parameters to a final state** with **H_2, U_2, V_2 and P parameters**, the change in enthalpy ΔH, can be calculated
  H = U + PV
- At initial state, $H_1 = U_1 + PV_1 \rightarrow (1)$
  At final state, $H_2 = U_2 + PV_2 \rightarrow (2)$
  $(2) - (1) \Rightarrow (H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$
  $\Delta H = \Delta U + P\Delta V \rightarrow (3)$
  As per first law of thermodynamics, $\Delta U = q + w$; $w = -P\Delta V$
  $\Delta H = q + w + P\Delta V$
  $\Delta H = q_p - P\Delta V + P\Delta V$
  $\Delta H = q_p \rightarrow (4)$
  q_p is the heat absorbed at constant pressure and is considered as heat content.
- Consider a closed system of gases which are chemically reacting to produce product gases at **constant temperature** and **pressure with V** and as the total volumes of the reactant and product gases respectively, and n_i and n_f are the number of moles of gaseous reactants and products. Then,
  For reactants: $P V_i = n_i RT$
  For products: $P V_f = n_f RT$
  Then considering reactants as initial state and products as final state,
  $P (V_f - V_i) = (n_f - n_i) RT$
  $P\Delta V = \Delta n_{(g)}RT$

$\Delta H = \Delta U + P\Delta V$

$\mathbf{\Delta H = \Delta U + \Delta n_{(g)}RT} \rightarrow (5)$

51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.

- The **Born – Haber** cycle is sued to determine the lattice enthalpy of NaCl as follows:



- ΔH_f = Heat of formation of sodium chloride = – 411.3 kJ mol^{-1}
  ΔH_1 = Heat of sublimation of Na(g) = 108.7 kJ mol^{-1}
  ΔH_2 = Ionisation energy of Na(g) = 495.0 kJ mol^{-1}
  ΔH_3 = Dissociation energy of $Cl_2(g)$ = 244 kJ mol^{-1}
  ΔH_4 = Electron affinity of Cl(S)= – 349.0 kJ mol^{-1}
- U = lattice energy of NaCl
  $\Delta H_f = \Delta H_1 + \Delta H_2 + \frac{1}{2}\Delta H_3 + \Delta H_4 + U$
  $\therefore U = (\Delta H_f) - (\Delta H_1 + \Delta H_2 + \frac{1}{2}\Delta H_3 + \Delta H_4)$s
- U = (–411.3) – (108.7 + 495.0 + 122 – 349)
  U = (–411.3) – (376.7)
  $\therefore$ U = – 788 kJ mol^{-1}
- This negative sign in lattice energy indicates that the **energy is released when sodium is formed from its constituent gaseous ions Na^+ and Cl^-**.

52. List the characteristics of Gibbs free energy.

- Gibbs free energy is defined as the part of **total energy of a system** that can be **converted** (or) **available for conversion into work**.
  G = H – TS
  where
  H = enthalpy, T = temperature and S = entropy
- G is a **state function** and is a **single value function**.
- **G** is an **extensive property**, whereas **ΔG** becomes **intensive property** for a **closed system**. Both G and ΔG values correspond to the system only.

53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

Given:

n = 2 moles
V_i = 500 ml = 0.5 lit
V_f = 2 lit
T = 25°C = 298 K

Formula used:

$w = -2.303\ nRT \log(\frac{V_f}{V_i})$

Solution:

w = -2.303 nRT log$\left(\frac{V_f}{V_i}\right)$

w = -2.303×2×8.314×298×log$\left(\frac{2}{0.5}\right)$

w = -2.303 x 2 x 8.314 x 298 x log(4)

w = -2.303 x 2 x 8.314 x 298 x 0.6021

w = -6871 J

$\boxed{w = -6.871\ kJ}$

54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1}. Calculate the enthalpy of combustion of the gas in kJ mol^{-1}.

Given:

T_i = 298 K
T_f = 298.45 K
k = 2.5 kJ K
m = 3.5g
M_m = 28

Formula used:

Heat evolved = k.ΔT

Solution:

ΔH_C = k (T_f – T_i)

ΔH_C = 2.5 kJ K (298.45 – 298) K^{-1}

ΔH_C = 1.125 kJ

$\Delta H_C = \frac{1.125}{3.5}$ x 28 kJ mol^{-1}

$\boxed{\Delta H_C = 9\ kJ\ mol^{-1}}$

55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C.

Given:

T_{sys} = 77°C = (77 + 273) = 350K
T_{sys} = 33°C = (33 + 273) = 306K
q = 245 J

Formula used:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

Solution:

$$\Delta S_{sys} = \frac{q}{T_{sys}} = \frac{-245}{350} = -0.7\ JK^{-1}$$

$$\Delta S_{surr} = \frac{q}{T_{sys}} = \frac{+245}{306} = +0.8\ JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = -0.7\ JK^{-1} + 0.8\ JK^{-1}$$

$\boxed{\Delta S_{univ} = 0.1\ JK^{-1}}$

56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.

Given:

n = 1 mole
P = 4.1 atm
V = 2Lit
T = ?
q = 3710 J

Formula used:

$$\Delta S = \frac{q}{T} = \frac{q}{\frac{PV}{nR}} = \frac{nRq}{PV}$$

Solution:

$$\Delta S = \frac{nRq}{PV}$$

$$\Delta S = \frac{1 \times 0.082 \times 3710}{4.1 \times 2}$$

$$\boxed{\Delta S = 37.10\ JK^{-1}}$$

57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 JK^{-1} mol^{-1}. Calculate the melting point of sodium chloride.

Given:

$\Delta H_f(NaCl)$ = 30.4 kJ = 30400 J mol^{-1}
$\Delta S_f\ (NaCl)$ = 28.4 JK^{-1} mol^{-1}
T_f = ?

Formula used:

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

Solution:

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

$$T_f = \frac{30400}{28.4}$$

$$\boxed{T_f = 1070.4\ K}$$

58. Calculate the standard heat of formation of propane, if its heat of combustion is −2220.2 kJ mol^{-1}. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 and −285.8 kJ mol^{-1} respectively.

Solution:

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
$\Delta H_C^o = -2220.2$ kJ mol^{-1} → (1)
$C + O_2 \rightarrow$ CO2
$\Delta H_f^o = -393.5$ kJ mol^{-1} → (2)
H2 + $\frac{1}{2} O_2 \rightarrow H_2O$
$\Delta H_f^o = -285.8$ kJ mol^{-1} → (3)
$3C + 4H_2 \rightarrow C_3H_8$
ΔH_C^o = ?
(2) × (3) => $3C + 3O_2 \rightarrow 3CO_2$
$\Delta H_f^o = -1180.5$ kJ → (4)
(3)× (4) ⇒ $4H_2 + 2O_2 \rightarrow 4H_2O$

$\Delta H_f^o = -1143.2\ kJ \rightarrow (5)$

$(4) + (5) - (1) \Rightarrow 3C + 3O_2 + 4H_2 + 2O_2 + 3CO_2 + 4H_2O \rightarrow 3CO_2 + 4H_2O + C_3H_8 + 5O_2$

$\Delta H_f^o = -1180.5 - 1143.2 = (-2220.2)\ kJ$

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H_f^o = -103.5\ kJ$

Standard heat of formation of propane is

$$\boxed{\Delta H_f^o (C_3H_8) = -103.5\ kJ}$$

59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S.No	Liquid	Boiling points (°C)	ΔH kJmol^{-1}
1	Ethanol	78.4	+42.4
2	Toluene	110.6	+35.2

For ethanol:

Given:

Tb = 78.4°C = (78.4 + 273) = 351.4 K

ΔH_V(ethanol) = + 42.4 kJ mol^{-1}

Formula used:

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

Solution:

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{42400}{351.4}$$

$$\boxed{\Delta S_V = +\ 120.66\ JK^{-1}mol^{-1}}$$

For toluene:

Given:

Tb = 110.6°C = (110.6 + 273) = 383.6 K

ΔSV (toluene) = + 35.2 KJ mol-1

Formula used:

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

Solution:

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{35200}{383.6}$$

$$\boxed{\Delta S_V = +\ 91.76\ JK^{-1}mol^{-1}}$$

60. For the reaction $Ag_2O(s) \rightarrow 2Ag(s)+1/2\ O_2(g)$: $\Delta H = 30.56$ kJ mol^{-1} and $\Delta S=6.66 JK^{-1}mol^{-1}$ (at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

Given:

$\Delta H = 30.56$ kJ mol^{-1}

$\Delta H = 30560$ J mol^{-1}

$\Delta S = 6.66 \times 10^{-3}$ kJ K^{-1} mol^{-1}

T = ? at which $\Delta G = 0$

Formula used:

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

$0 = \Delta H - T\Delta S$

$T = \frac{\Delta H}{\Delta S}$

Solution:

$T = \frac{\Delta H}{\Delta S}$

$T = \frac{30.56}{6.66\times10^{-3}}$

$T = 4589K$

i) At 4589K ; $\Delta G = 0$, the reaction is in **equilibrium**.

ii) At temperature below 4598 K, $\Delta H > T\,\Delta S$. $\Delta G = \Delta H - T\Delta S > 0$, the reaction in the forward direction, is non-spontaneous. In other words the reaction occurs in the **backward direction.**

61. What is the equilibrium constant Keq for the following reaction at 400K.
$2NOCl\,(g) \rightleftharpoons 2NO(g) + Cl_2(g)$,
given that $\Delta H^o = 77.2kJ\ mol^{-1}$;
and $\Delta S^o = 122JK^{-1}mol^{-1}$.

Given:

$T = 400$ K ; $\Delta H° = 77.2$ kJ mol^{-1} = 77200 J mol^{-1};
$\Delta S° = 122$ JK-1 mol^{-1}

Formula used:

$\Delta G° = -2.303\ RT \log K_{eq}$

$\log K_{eq} = \frac{\Delta G°}{-2.303RT}$

$\log K_{eq} = \frac{\Delta H° - T\Delta S°}{-2.303RT}$

Solution:

$\log K_{eq} = \frac{\Delta H° - T\Delta S°}{-2.303RT}$

$\log K_{eq} = \frac{7720 - 400\times122}{-2.303\times8.314\times400}$

$\log K_{eq} = -\frac{28400}{7659}$

$\log K_{eq} = -3.7080$

K_{eq} = antilog (-3.7080)

$\boxed{K_{eq} = 1.95 \times 10^{-4}}$

62. Cyanamide (NH_2CN) is completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be −742.4 kJ mol^{-1}, calculate the enthalpy change of the reaction at 298K. $NH_2CN(s) + 3/2\ O2(g) \rightarrow N_2\,(g) + CO_2\,(g) + H_2O(l)$ ΔH= ?

Given:

T = 298K

ΔU = -742.4 kJ mol-1

ΔH = ?

Formula used:

$\Delta H = \Delta U + \Delta n_{(g)}RT$

$\Delta H = \Delta U + (n_p - n_r)\ RT$

Solution:

$\Delta H = \Delta U + (n_p - n_r)\ RT$

$\Delta H = -742.4 + [2 - \frac{3}{2}] \times 8.314 \times 10^{-3} \times 298$

$\Delta H = -742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$

$\Delta H = -742.4 + 1.24$

$$\boxed{\Delta H = -741.16 \text{ kJ mol}^{-1}}$$

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C − H, C − C , C = C and H − H are 414, 347, 618 and 435 kJ mol^{-1}.

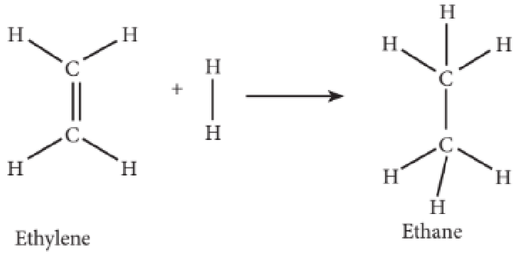
Given:

$E_{C\text{-}H} = 414 \text{ kJ mol}^{-1}$
$E_{C\text{-}H} = 347 \text{ kJ mol}^{-1}$
$E_{C\text{-}H} = 618 \text{ kJ mol}^{-1}$
$E_{H\text{-}H} = 435 \text{ kJ mol}^{-1}$

Formula used:

$\Delta H_r = \sum(\text{Bond energy})_r - \sum(\text{Bond energy})_P$

Solution:



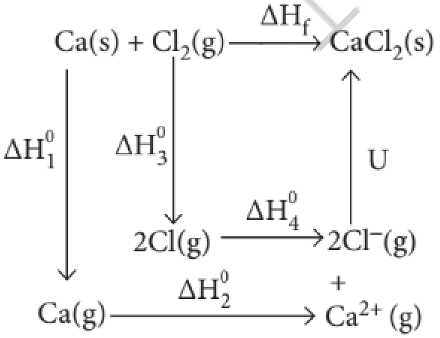
$\Delta H_r = (E_{C=C} + 4E_{C\text{-}H} + E_{H\text{-}H}) - (E_{C\text{-}C} + 6E_{C\text{-}H})$
$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$
$\Delta H_r = 2709 - 2831$

$$\boxed{\Delta H_r = -122 \text{ kJ mol}^{-1}}$$

64. Calculate the lattice energy of $CaCl_2$ from the given data

$Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)}$ $\Delta H_f^0 = -795$ KJ mol^{-1}
Sublimation : $Ca_{(s)} \rightarrow Ca_{(g)}$ $\Delta H_1° = +121$ KJ mol^{-1}
Ionization : $Ca_{(g)} \rightarrow Ca^{2+}_{(g)} + 2e^-$ $\Delta H_2° = +242.8$ KJ mol^{-1}
Dissociation : $Cl_{2(g)} \rightarrow 2\,Cl_{(g)}$ $\Delta H_3° = +242.8$ KJ mol^{-1}
Electron affinity : $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ $\Delta H_3° = -355$ KJ mol^{-1}

Solution:



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + 2\Delta H_4 + u$
$-795 = 121 + 2422 + 242.8 + (2 \times -355) + u$
$-795 = 2785.8 - 710 + u$
$-795 = 2075.8 + u$
$u = -795 - 2075.8$

$$\boxed{u = -2870.8 \text{ kJ mol}^{-1}}$$

65. Calculate the enthalpy change for the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ from the following data.
$2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$; $\Delta H = -741$ kJ
$C + 1/2\ O_2 \rightarrow CO$; $\Delta H = -137$ kJ
$C + O_2 \rightarrow CO_2$ $\Delta H = -394.5$ kJ

Given:
$\Delta H_f\ (Fe_2O_3) = -741\ kJ\ mol^{-1}$
$\Delta H_f(CO) = -137\ kJ\ mol^{-1}$
$\Delta H_f(CO_2) = -394.5\ kJ\ mol^{-1}$
$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2\ \Delta Hr = ?$

Formula used:
$\Delta Hr = \sum(\Delta H_f)_{products} - \sum(\Delta H_f)_{reactants}$

Solution:
$\Delta Hr = \sum(\Delta H_f)_{products} - \sum(\Delta H_f)_{reactants}$
$\Delta Hr = [2\ \Delta H_f(Fe) + 3\ \Delta H_f(CO_2)] - [\Delta H_f(Fe_2O_3) + 3\Delta H_f(CO)]$
$\Delta Hr = [0 + 3\ (-394.5)\ ] - [-741 + 3\ (-137)]$
$\Delta Hr = [-\ 1183.5\ ] - [-1152]$
$\Delta Hr = -\ 1183.5 + 1152$

$$\boxed{\Delta Hr = -31.5\ KJ\ mol^{-1}}$$

66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A) , 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate ΔG^o for the following equilibria.
$B \rightleftharpoons A$ ΔG_1^o?
$B \rightleftharpoons C$ ΔG_2^o?

Given:
T = 175°C = 175 + 273 = 448 K
Concentration of 1 – pentyne [A] = 1.3%
Concentration of 2 – pentyne [B] = 95.2%
Concentration of 1, 2 – pentadiene [C] = 3.5%

Formula used:
$\Delta G° = -2.303\ RT \log K_{eq}$

Solution:
At equilibrium
$B \rightleftharpoons A$
$95.2\%\ 1.3\% \Rightarrow K_1 = \frac{1.3}{95.2} = 0.0136$
$B \rightleftharpoons C$
$95.2\%\ 3.5\% \Rightarrow K_1 = \frac{3.5}{95.2} = 0.0367$
$\Rightarrow \Delta G_1° = -2.303\ RT \log K_1$
$\Delta G_1° = -\ 2.303 \times 8.3\ 14 \times 448 \times \log 0.0136$
$\Delta G_1° = +\ 16010\ J$

$$\boxed{\Delta G_1° = +\ 16\ kJ}$$

$\Rightarrow \Delta G_2° = -\ 2.303\ RT \log K_2$
$\Delta G_2° = -2.303 \times 8.314 \times 448 \times \log 0.0367$
$\Delta G_2° = +\ 12312\ J$

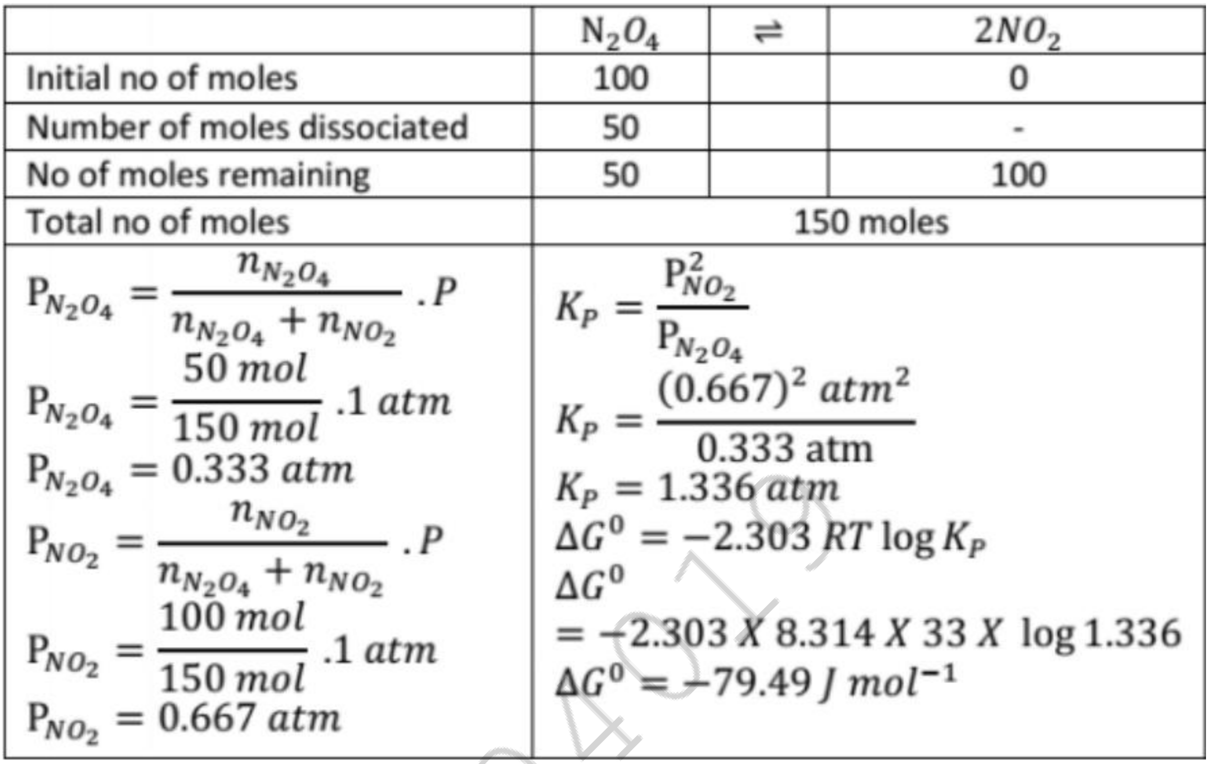
$$\boxed{\Delta G_2° = +12.312\ kJ}$$

67. At 33K, N_2O_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution:

T = 33K

$N_2O_4 \rightleftharpoons 2NO_2$



	N_2O_4	⇌	$2NO_2$
Initial no of moles	100		0
Number of moles dissociated	50		-
No of moles remaining	50		100
Total no of moles	150 moles		
$P_{N_2O_4} = \frac{n_{N_2O_4}}{n_{N_2O_4} + n_{NO_2}} .P$ $P_{N_2O_4} = \frac{50\ mol}{150\ mol} .1\ atm$ $P_{N_2O_4} = 0.333\ atm$ $P_{NO_2} = \frac{n_{NO_2}}{n_{N_2O_4} + n_{NO_2}} .P$ $P_{NO_2} = \frac{100\ mol}{150\ mol} .1\ atm$ $P_{NO_2} = 0.667\ atm$	$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}}$ $K_P = \frac{(0.667)^2\ atm^2}{0.333\ atm}$ $K_P = 1.336\ atm$ $\Delta G^0 = -2.303\ RT \log K_P$ ΔG^0 $= -2.303\ X\ 8.314\ X\ 33\ X\ \log 1.336$ $\Delta G^0 = -79.49\ J\ mol^{-1}$		

68. The standard enthalpies of formation of SO_2 and SO_3 are −297 kJ mol^{-1} and −396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction: SO2 + 1/2 $O_2 \rightarrow SO_3$

Given:

$\Delta H_f°(SO_2) = – 297$ KJ mol^{-1}

$\Delta H_f°(SO_2) = – 297$ KJ mol^{-1}

$SO_2 + ½\ O_2 \rightarrow SO_3\ \Delta H_r° = ?$

Formula used:

$\Delta H_r° = (\Delta H_f°)_{compound} – \sum(\Delta H_f°)_{elements}$

$\Delta H_r° = \Delta H_f°\ (SO_3) – [\Delta H_f°\ (SO_2) + 12\ \Delta H_f°\ (O_2)]$

Solution:

$\Delta H_r° = (\Delta H_f°)_{compound} – \sum(\Delta H_f°)_{elements}$

$\Delta H_r° = \Delta H_f°\ (SO_3) – [\Delta H_f°\ (SO_2) + 12\ \Delta H_f°\ (O_2)]$

$\Delta H_r° = – 396$ kJ mol^{-1} – (- 297 kJ mol^{-1} + 0)

$\Delta H_r° = – 396$ kJ mol^{-1}+297

$$\boxed{\Delta H_r° = – 99\ kJmol^{-1}}$$

69. For the reaction at 298 K: 2A +B → C, ΔH=400 kJ mol^{-1} ; ΔS = 0.2 kJK^{-1} mol^{-1} Determine the temperature at which the reaction would be spontaneous.

Given:

T = 298K

ΔH = 400 J mol^{-1}

$\Delta S = 0.2\ J\ K^{-1}\ mol^{-1}$

Formula used:

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

Solution:

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

If T = 2000K, $\Delta G = 400 - (0.2 \times 2000) = 0$

If T > 2000 K, $\Delta H = 400 kJmol^{-1}$

ΔG will be **negative**.

The reaction would be **spontaneous only beyond 2000 K**.

70. Find out the value of equilibrium constant for the following reaction at 298K, $2NH_3(g) + CO_3(g) \rightleftharpoons NH_2CONH_2\ (aq) + H_2O\ (l)$ Standard Gibbs energy change, ΔG_r^o at the given temperature is –13.6 kJ mol^{-1}.

Given:

T = 298 K

$\Delta G_r° = -13.6\ kJ\ mol^{-1} = -13600\ J\ mol^{-1}$

Formula used:

$\Delta G° = -2.303\ RT \log K_{eq}$

$\log K_{eq} = \frac{\Delta G°}{-2.303RT}$

Solution:

$\log K_{eq} = \frac{\Delta G°}{-2.303RT}$

$\log K_{eq} = -\frac{13,6}{2.303 \times 8.314 \times 10^{-3} \times 298}$

$\log K_{eq} = 2.38$

$K_{eq} = \text{antilog}\ (2.38)$

$$\boxed{K_{eq} = 239.88}$$

71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbondioxide. Find out the amount of heat evolved in kJ, during this combustion. ($\Delta H_C(CH_4) = -890\ kJ\ mol^{-1}$ and ($\Delta H_C(C_2H_4) = -1423\ kJ\ mol^{-1}$

Given:

$\Delta H_C\ (CH_4) = -890\ kJ\ mol^{-1}$

$\Delta H_C\ (C_2H_4) = -1423\ kJ\ mol^{-1}$

Solution:

Let the mixture contain x lit of CH_4 and (3.67 – x) lit of ethylene.

$CH_4\ (x\ lit) + 2O_2 \rightarrow CO_2\ (x\ lit) + 2H_2O$

$C_2H_4\ [(3.67 - x)\ lit] + 3O_2 \rightarrow 2CO_2\ [2(3.67 - x)\ lit] + 2H_2O$

Volume of carbon dioxide formed x + 2 (3.67 – x) 6.11 lit

x + 7.34 – 2x = 6.11

x = 1.23 lit

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$\Delta H_c = \left[\frac{\Delta H_C(CH_4)}{22.4} \times\ x\right] + \left[\frac{\Delta H_C(C_2H_4)}{22.4} \times (3.67 - x)\right]$

$\Delta H_c = \left[\frac{-890}{22.4} \times\ 1.23\right] + \left[\frac{1423}{22.4} \times (3.67 - 1.23)\right]$

$\Delta H_c = [-48.87 kJmol^{-1}] + [-155 kJmol^{-1}]$

$$\boxed{\Delta H_c = -203.87\ kJ\ mol^{-1}}$$