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UNIT – 1 ENTROPY AND SECOND LAW OF THERMODYNAMICS

B.SC. SEM - V

SUBJECT CODE : US05CCHE23

TITLE OF PAPER : PHYSICAL CHEMISTRY

CYCLIC PROCESS

- ❑ WHEN A SYSTEM COMPLETES A SERIES OF CHANGES AND ULTIMATELY RETURNS TO ITS ORIGINAL STATE, IT IS KNOWN TO HAVE COMPLETED ONE CYCLE. THE ENTIRE PROCESS OF CHANGES IS KNOWN AS A CYCLIC PROCESS.
- ❑ SINCE THE INTERNAL ENERGY OF A SYSTEM DEPENDS ONLY UPON ITS STATE, IT FOLLOWS THAT IN A CYCLIC PROCESS, THE NET CHANGE OF INTERNAL ENERGY IS ZERO, I.E.,

ACCORDING TO FIRST LAW OF THERMODYNAMICS; $\Delta E = 0 = Q - W$

$$Q = W$$

- ❑ IF A SERIES OF CHANGES ARE CONDUCTED AT A CONSTANT TEMPERATURE, THE CYCLE IS KNOWN AS AN ISOTHERMAL CYCLE.
- ❑ IF THE CHANGES ARE CARRIED OUT REVERSIBLY, THEN THE CYCLE IS KNOWN AS A REVERSIBLE CYCLE.
- ❑ THE MOST WELL KNOWN CYCLIC PROCESS IS CARNOT'S CYCLE.

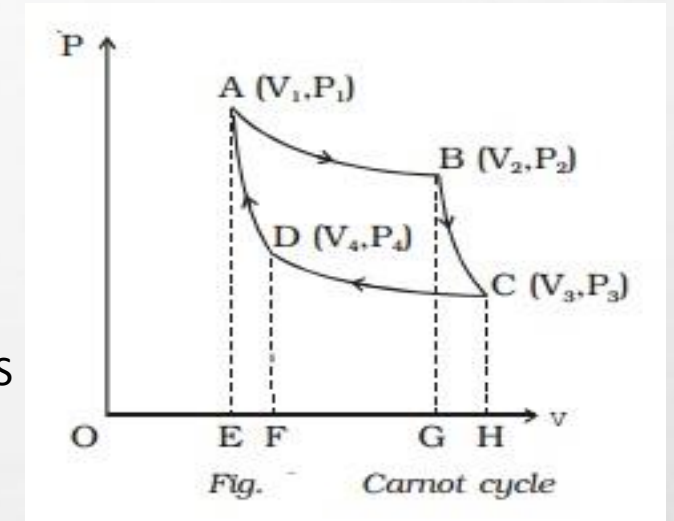
CARNOT CYCLE

- THE SYSTEM CONSISTS OF ONE MOLE OF AN IDEAL GAS WHICH IS SUBJECTED TO A SERIES OF FOUR SUCCESSIVE OPERATIONS KNOWN AS FOUR STROKES.

(I) STROKE 1 :- ISOTHERMAL EXPANSION

- THE GAS IS ALLOWED TO EXPAND REVERSIBLY AND ISOTHERMALLY AT THE TEMPERATURE T_2 SO THAT THE VOLUME INCREASES FROM V_1 TO V_2 (POINT A TO B).
- EXPANSION IS ISOTHERMAL, SO $\Delta U = 0$.
- ACCORDING TO FIRST LAW OF THERMODYNAMICS; $\Delta U = Q - W \therefore Q = W$, I.E. THE HEAT ABSORBED BY THE SYSTEM IS EQUAL TO THE WORK DONE BY THE SYSTEM ON THE SURROUNDINGS. SUPPOSE HEAT ABSORBED IS q_z AND WORK DONE IS W_1 THEN

$$q_z = W_1 = RT_2 \ln (V_2/V_1) \text{ _____ (1)}$$



(II) STROKE 2 :- ADIABATIC EXPANSION

- THE GAS IS ALLOWED TO EXPAND REVERSIBLY AND ADIABATICALLY FROM THE VOLUME V_2 TO V_3 I.E. FROM POINT B TO C. HERE HEAT IS NOT ABSORBED, SO THE TEMPERATURE FALLS FROM T_2 TO T_1 . $Q = 0$, SO $\Delta U = -W$.
- SINCE THE WORK IS DONE BY THE SYSTEM ON THE SURROUNDINGS BY CONVENTION, W IS NEGATIVE.

$$\therefore \Delta U = -W$$

- NOW, $C_v = (\sigma U / \sigma T)_v$ _____(2)

$$\therefore \Delta U = C_v \Delta T = C_v (T_1 - T_2) = -W \quad \text{_____}(3)$$

$$W = C_v (T_2 - T_1) \quad \text{_____}(4)$$

- IF WORK W IS DENOTED BY W_2 , THEN

$$W_2 = C_v (T_2 - T_1) \quad \text{_____}(5)$$

(III) STROKE 3 :- ISOTHERMAL COMPRESSION

- THE GAS IS SUBJECTED TO A REVERSIBLE AND ISOTHERMAL COMPRESSION AT TEMPERATURE T_1 .
- THE VOLUME DECREASES FROM V_3 TO V_4 . I.E. FROM POINT C TO D.
- IN THIS CASE WORK IS DONE ON THE SYSTEM SO HEAT IS PRODUCED AND GIVEN UP TO THE SURROUNDINGS.
- PROCESS IS ISOTHERMAL AND REVERSIBLE SO, $\Delta U = 0$.
- IF HEAT IS DENOTED BY q_1 AND WORK BY w_3

$$- q_1 = -w_3 = RT_1 \ln (V_4/V_3) \quad \text{_____} (6)$$

(IV) STROKE 4 :- ADIABATIC COMPRESSION

- THE GAS IS SUBJECTED TO A REVERSIBLE AND ADIABATIC COMPRESSION.
- THE VOLUME DECREASES FROM V_4 TO V_1 . I.E. FROM POINT D TO A.
- WORK IS DONE ON THE SYSTEM, HENCE W IS POSITIVE.
- $Q = 0$, SO $\Delta U = Q - W = W = -C_v (T_2 - T_1)$
- IF W IS DENOTED BY W_4 THEN,

$$W_4 = -C_v (T_2 - T_1) \quad \text{_____} (7)$$

- THE NET HEAT ABSORBED BY THE SYSTEM IS

$$\begin{aligned} Q &= Q_2 + (-Q_1) = RT_2 \ln(V_2/V_1) + RT_1 \ln(V_4/V_3) \\ &= RT_2 \ln(V_2/V_1) - RT_1 \ln(V_3/V_4) \end{aligned} \quad \text{_____ (8)}$$

- NOW, $V_3/V_2 = V_4/V_1$ OR $V_2/V_1 = V_3/V_4$ _____ (9)

$$\therefore Q = Q_2 - Q_1 = R (T_2 - T_1) \ln(V_2/V_1) \quad \text{_____ (10)}$$

- SIMILARLY, THE NET WORK DONE BY THE GAS IS

$$\begin{aligned} W &= W_1 + W_2 + W_3 + W_4 \\ &= RT_2 \ln(V_2/V_1) - C_v (T_2 - T_1) + RT_1 \ln(V_4/V_3) + C_v (T_2 - T_1) \\ &= RT_2 \ln(V_2/V_1) - RT_1 \ln(V_3/V_4) \end{aligned} \quad \text{_____ (11)}$$

- SINCE; $V_2/V_1 = V_3/V_4$
 $W = R (T_2 - T_1) \ln(V_2/V_1) \quad \text{_____ (12)}$

- FROM EQUATION (10) AND (12), $Q = W$
- THUS, THE ESSENTIAL CONDITION FOR A CYCLIC PROCESS THAT THE NET WORK DONE IS EQUAL TO THE NET HEAT ABSORBED WHICH IS FULLY SATISFIED.
- THE RELATION BETWEEN W , THE NET WORK DONE BY THE SYSTEM AND Q_2 THE QUANTITY OF HEAT ABSORBED AT A HIGHER TEMPERATURE T_2 IS OBTAINED BY DIVIDING EQUATION (12) BY (1)

$$W = Q_2 (T_2 - T_1)/T_2 \quad \text{_____}(13)$$

- SINCE $(T_2 - T_1)/T_2 < 1$, $W < Q_2$.

- THUS, WORK DONE IS LESS THAN THE HEAT ABSORBED.
- THIS MEANS THAT ONLY A PART OF THE HEAT IS ABSORBED BY THE SYSTEM AT THE HIGHER TEMPERATURE T_2 IS TRANSFORMED INTO WORK.
- THE REST OF THE HEAT Q_1 IS GIVEN TO THE SURROUNDING AT THE TEMPERATURE T_1 .



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