Nernst Heat Theorem
Third Law of Thermodynamics
Residual Entropy

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Nernst Heat Theorem

Richards, measured ΔG for a cell reaction at different temperatures by measuring e.m.f. of the cell and found that $[\frac{\partial(\Delta G)}{\partial T}]_P$ decreases with decrease in temperature. On the basis of Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T.[\frac{\partial(\Delta G)}{\partial T}]_P$$

Which is applicable for any process including a chemical reaction, he concluded that as temperature decreases values of ΔG and ΔH approach closer to each other. Nernst, later on, broadened this concept and suggested that

"As temperature is lowered towards absolute zero, value of $[\frac{\partial(\Delta G)}{\partial T}]_P$ decreases towards zero, and at absolute zero temperature approaches zero."

This is known as Nernst Heat Theorem.

Mathematical Statement:

As $T \to 0$ K, $[\frac{\partial(\Delta G)}{\partial T}]_P \to 0$ and at $T = 0$ K

$[\frac{\partial(\Delta G)}{\partial T}]_P = 0$ and $\Delta G = \Delta H$

Thus,

$$\lim_{T=0}[\frac{\partial(\Delta G)}{\partial T}]_P = \lim_{T=0}[\frac{\partial(\Delta H)}{\partial T}]_P = 0$$

From thermodynamics, we know that

$[\frac{\partial(\Delta G)}{\partial T}]_P = -\Delta S$

And, $[\frac{\partial(\Delta H)}{\partial T}]_P = \Delta C_P$

Where ΔS = Change in entropy in a chemical reaction

ΔC_P = Change in Heat capacity in a chemical reaction

For example, consider a chemical reaction

$$aA + bB \rightarrow mM + nN$$

for which,

$$\Delta S = (m.S_M + n.S_N) - (a.S_A + b.S_B)$$

$$\Delta C_P = [m.(C_P)_M + n.(C_P)_N] - [a.(C_P)_A + b.(C_P)_B]$$

$\therefore$ It follows from Nernst Heat Theorem that

$$\lim_{T \to 0K} \Delta S = 0$$

$$\lim_{T \to 0K} \Delta C_P = 0$$

Nernst Heat Theorem holds good only in the case of solids.

Extension of Nernst Heat Theorem:

According to Nernst Heat Theorem:

$$\lim_{T \to 0K} \Delta C_P = 0$$

This implies that at absolute zero temperature change in heat capacity for a chemical reaction will be zero. Thus, at absolute zero temperature

Sum of heat capacities of reactants = Sum of heat capacities of products

Experimentally, it is known that heat capacity of solid decreases with lowering of temperature. Einstein's theory of heat capacities, Debye's theory of heat capacities and Free electron model of metals, proposed to explain it, predicted that as T → 0K, heat capacity of solids approaches zero. Combining this with the result

of Nernst Heat Theorem as stated above, it may be stated that C_P of all solid substances at 0K equals zero. Thus, Nernst Heat Theorem may be extended and written as

$$\lim_{T \to 0K} C_P = 0$$

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THIRD LAW OF THERMODYNAMICS

Extension of Nernst Heat Theorem leads to a conclusion that

$$\lim_{T \to 0K} \Delta S = 0$$

This implies that at absolute zero temperature, ΔS for a process including a chemical reaction involving solid substances, becomes zero. At absolute zero temperature applying this concept on the following reactions lead to the conclusion:

(i) $A(s) \rightarrow B(s)$

$S_A = S_B$

(ii) $aA(s) + bB(s) \rightarrow mM(s) + nN(s)$

$m.S_M + n.S_N = a.S_A + b.S_B$

This is possible only when entropy of all solid substances at absolute zero temperature is taken zero.

$$\lim_{T \to 0K} S \text{ ⍰ } 0$$

This conclusion led the enunciation of the Third law of thermodynamics which states that

Statement I: “At absolute zero temperature, entropy of every substance may become zero and it becomes zero in the case of a perfectly crystalline structure.”

Statement II: “Entropy of every pure perfect crystalline substance is zero at absolute zero temperature.”

Statement III: “Every substance has finite positive entropy at a temperature and its entropy decreases with lowering of temperature, and may become zero at absolute zero temperature, and entropy is definitely zero at absolute zero temperature if the substance is pure perfect crystalline solid.”

RESIDUAL ENTROPY

Entropy of a substance at a particular temperature is known as "absolute entropy" of the substance for that temperature. If absolute entropy of a substance is determined from thermal method using Third law of thermodynamics, it is called THERMAL ENTROPY. If absolute entropy of a substance is determined using statistical mechanics, it is called STATISTICAL ENTROPY. At a temperature, statistical entropy of a substance is found somewhat greater than its thermal entropy.

According to the Third law of thermodynamics, absolute entropy of a substance at 0K, i.e., at absolute zero temperature, should be zero. But, experimentally, on the basis of thermal methods, absolute entropy of a substance at 0K is found to be finite. This finite value of entropy of a substance at 0K, is called RESIDUAL ENTROPY.

The existence of residual entropy in a crystal at 0K, is assumed to be due to the possible alternative arrangements of molecules in the solid.

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