Determination of Absolute Entropy of a substance from Thermal measurements

For

B.Sc. Chemistry Honours Part - II

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Determination of Absolute Entropy of a substance from Thermal measurements

If absolute entropy of a substance at a particular temperature is determined by thermal method, it is called THERMAL ENTROPY. Thermal methods used to determine Absolute Entropy are: Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). From any of these methods, molar heat capacity of the substance is determined at various temperatures between desired temperature and possible temperature nearest to Absolute Zero. Then, using graphical technique, absolute entropy of the substance at the desired temperature is evaluated.

Variation of entropy with temperature

Consider an infinitesimally small change in state of a system or a substance at temperature, T Kelvin (K). Change in entropy due to this process may be given by

$$dS = \frac{dq}{T}$$

Where dq is the heat change taken place due to state change at temperature, TK.

If this process takes place at constant pressure then

$$dS = \frac{dq_P}{T}$$

Dividing both sides by dT we get:

$$\frac{dS}{dT} = \left[\frac{dq_P}{dT}\right] X \frac{1}{T}$$

$$\frac{dS}{dT} = C_P X \frac{1}{T}$$

$$dS = \frac{C_P}{T} X dT$$

Where $\left[\frac{dq_P}{dT}\right]$ **=** C_P **= Molar Heat Capacity of the substance**

On Integration between T = 0K, S = 0 and T = T K, S = S_T **we get:**

$$\int_0^{S_T} dS = \int_0^T \frac{C_P}{T} . dT$$

$$[S]_0^{S_T} = \int_0^T \frac{C_P}{T} . dT$$

$$[S_T - 0] = \int_0^T \frac{C_P}{T} . dT$$

$$\therefore \quad S_T = \int_0^T \frac{C_P}{T} . dT$$

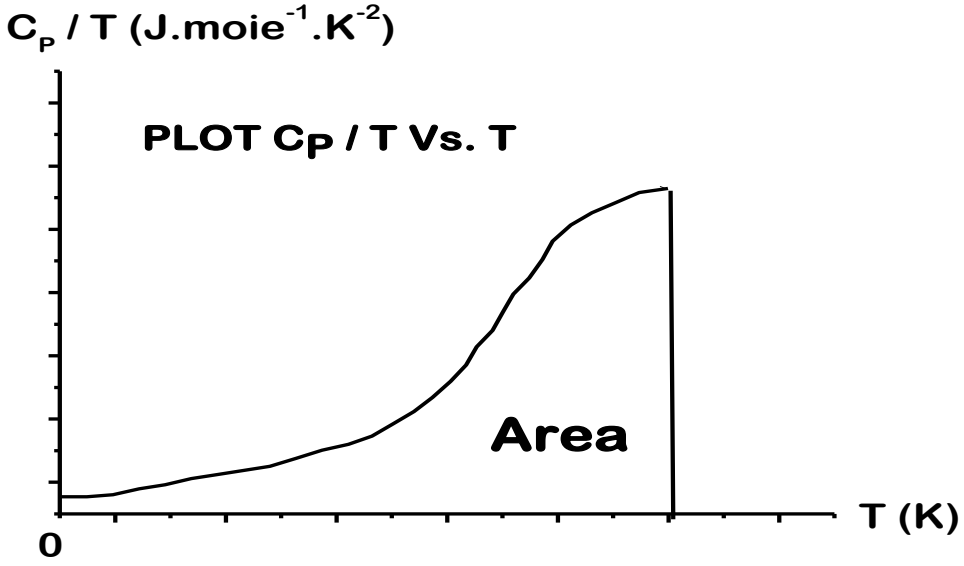
$$\therefore \quad S_T = [Area\ under\ graph\ in\ plot\ \frac{C_P}{T}\ Vs.T]_0^T$$

$$\therefore \quad S_T = Area\ under\ graph\ in\ plot\ \frac{C_P}{T}\ Vs.T\ between\ 0K\ and\ TK$$

Where S_T **is the absolute entropy of the substance at T K.**

Method and Evaluation:

In order to determine absolute entropy of a substance at a temperature TK, molar heat capacities C_P of the substance are determined at various temperatures T K to temperature as low as possible nearer to 0K using any of the thermal methods. Then a graph $\frac{C_P}{T}\ Vs.T$ is plotted, and the graph obtained is extrapolated upto T = 0K.



Area under graph between 0 and T K in plot $\frac{C_P}{T}\ Vs.T$ is evaluated which gives absolute entropy, S_T of the substance at TK.

Recommended Books:

1. **Thermodynamics for Chemists by SAMUEL GLASSTONE**
2. **Physical Chemistry by ATKINS**
3. **Principles of Physical Chemistry by SAMUEL H. MARON & CARL F. PRUTTON**
4. **Principles of Physical Chemistry by PURI, SHARMA, & PATHANIA**
5. **Chemistry for Degree Students B.Sc. Second Year by Dr.R.L.Madan**

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