

**S. S. College. Jehanabad (Magadh University)**

**Department : Physics**

**Subject : Thermodynamics**

**Class : B.Sc( H) Physics Part I**

**Topic: Application of Maxwell's Thermodynamical Relation**

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## Introduction

Out of several properties of a thermodynamic system some of these like internal energy and entropy cannot be measured. So thermodynamic relations can relate these properties with those that can be measured like pressure, temperature, compressibility etc. In thermodynamic relations un-measurable properties can be written as partial derivatives involving both intensive and extensive variables. A thermodynamical relation is a rule which is obtained by a simple thermodynamic reasoning and applies to most of the systems. The usefulness of the above relations lies in the fact that they relate quantities which seem unrelated. They help us to link data obtained in various ways or replace a difficult measurement by another one. They can also be used to obtain values of one variable from the calculations of another variable. These relations are very general and immensely useful as they simplify analysis of thermodynamic systems. The most convenient way to derive these relations is to use partial differentiation.

## Applications

### 1. Specific Heat Equation

The specific heat at constant pressure is given by

$$\begin{aligned}C_p &= \left( \frac{\partial Q}{\partial T} \right)_P \\&= T \left( \frac{\partial S}{\partial T} \right)_P \quad (\because \partial Q = T \cdot \partial S)\end{aligned}$$

the specific heat at constant volume is

$$\begin{aligned}C_v &= \left( \frac{\partial Q}{\partial T} \right)_V \\&= T \left( \frac{\partial S}{\partial T} \right)_V\end{aligned}$$

if entropy  $S$  is taken as a function of  $T$  and  $V$  and since  $dS$  is a perfect differential,

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

$$\left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial S}{\partial T} \right)_V \left( \frac{\partial T}{\partial T} \right)_P + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

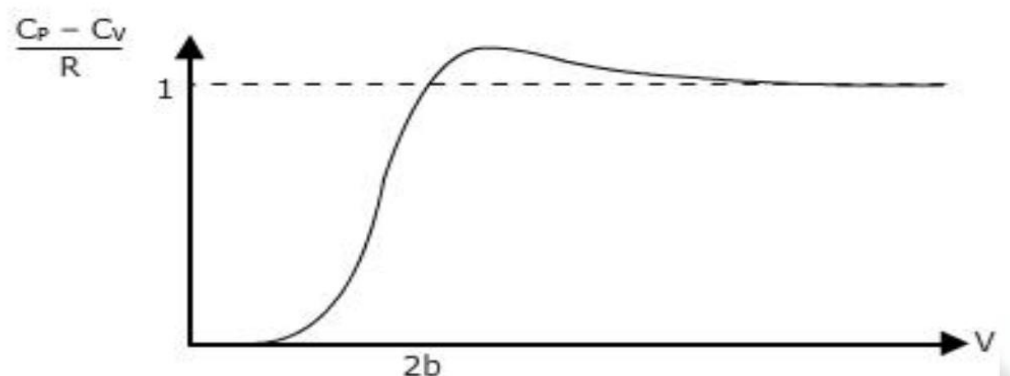
$$T \left( \frac{\partial S}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_V + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{(From Maxwell's second relation)}$$

$$T \left( \frac{\partial S}{\partial T} \right)_P - T \left( \frac{\partial S}{\partial T} \right)_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \quad \dots\dots\dots (1)$$

**(a) For a perfect gas :**



The equation of state for one mole of a perfect gas is

$$PV = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

equation (1) takes the form

$$C_P - C_V = T \left(\frac{R}{V}\right) \left(\frac{R}{P}\right)$$

$$= \frac{R^2 T}{PV}$$

$$= \frac{R^2 T}{RT}$$

$$C_P - C_V = R$$