(*i*) $x$ is said to be

(*ii*) $x$ is said to be intensive variable, if

An extensive variable may become an intense variable by specifying unit amount of

Thus, mass and volume are extensive variables but density $\left(\frac{M}{V}\right)$ and specific volume

intensive variables. Similarly heat capacity is extensive variable but specific heat is an

variable. The extensive and intensive variables of some systems are given in Table 6.1

**TABLE 6.1**

| *System* | *Extensive Variable* | | *Intensive Variable* | |
|---|---|---|---|---|
| Chemical system | Volume | V | Pressure | P |
| Stretched wire | Length | L | Tension | F |
| Surface film | Area | A | Surface tension | T |
| Electric cell | Charge | Q | E.M.F. | E |
| Paramagnetic solid | Magnetisation | I | Magnetic intensity | H |

## 6.3 Maxwell's Thermodynamical Relations (General Relationsh

From the first and second law of thermodynamics, Maxwell was able to derive six fundam thermodynamical relations. The state of a system can be specified by any pair of quantiti pressure ($P$), volume ($V$), temperature ($T$), and entropy ($S$). In solving any thermodynamical pr the most suitable pair is chosen and the quantities constituting the pair are taken as indep variables.

From the first law of thermodynamics,

$$\delta Q = dU + \delta W$$

$$\delta Q = dU + PdV$$

or

$$dU = \delta Q - PdV$$

For the second law of thermodynamics,

$$dS = \frac{\delta Q}{T}$$

or $$\delta Q = TdS$$

Substituting this value of $\delta Q$, we get

$$\delta U = TdS - PdV \qquad ...(6.1)$$

Considering $U$, $S$ and $V$ to be function of two independent variables $x$ and $y$ [here, in general, $x$ and $y$ can be any two variables out of $P$, $V$, $T$ and $S$],

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

and $$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in equation (6.1), we get

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_y dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right) dy\right]$$

$$= \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_x\right] dx + \left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right] dy$$

Comparing the coefficients of $dx$ and $dy$, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad ...(6.2)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \qquad ...(6.3)$$

Differentiating equation (6.2) with respect to $y$ and equation (6.3) with respect to $x$,

$$\frac{\partial^2 U}{\partial y.\partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y.\partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial V.\partial x}$$

and $$\frac{\partial^2 U}{\partial x.\partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x.\partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x.\partial y}$$

The change in internal energy brought about by changing $V$ and $T$, whether $V$ is changed by $dV$ first and $T$ by $dT$ later or vice versa is the same.

It means $dU$ is a perfect differential.

$\therefore$ $$\frac{\partial^2 U}{\partial y.\partial x} = \frac{\partial^2 U}{\partial x.\partial y}$$ and

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 x}{\partial y.\partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y.\partial x}$$

$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right) + T\frac{\partial^2 S}{\partial x} - \left(\frac{\partial P}{\partial}\right)\left(\frac{\partial V}{\partial}\right) - P\frac{\partial^2 V}{\partial}$$

Since $dS$ and $dV$ are also perfect differentials, we have

$$\frac{\partial^2 S}{\partial x.\partial y} = \frac{\partial^2 S}{\partial y.\partial x} \quad \text{and} \quad \frac{\partial V}{\partial x.\partial y} = \frac{\partial V}{\partial y.\partial x}$$

Equation (6.4), therefore reduces to

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x$$

This is the general expression for Maxwell's thermodynamical relations. In place of the indep variables $x$ and $y$, any two of the four variables $S$, $T$, $P$ and $V$ can be substituted so that there one mechanical variable ($P$ or $V$) and one thermal variable ($S$ or $T$). Thus, there may be four possible substitutions ($S$, $V$), ($T$, $V$), ($S$, $P$) and ($T$, $P$), providing the four Maxwell's thermodyn relations.

## First Relation:

Put $x = S$ and $y = V$ in equation (6.5), so that

$$\frac{\partial S}{\partial x} = 1 \quad , \quad \frac{\partial V}{\partial y} = 1$$

and

$$\frac{\partial S}{\partial y} = 0 \quad , \quad \frac{\partial V}{\partial x} = 0$$

Substituting in equation (6.5), we get

$$\left(\frac{\partial T}{\partial y}\right)_x = -\left(\frac{\partial P}{\partial x}\right)_y$$

But $\partial y = \partial V$ (as $y = V$) and $\partial s = \partial S$ (as $x = S$). Hence

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(i$$

This is Maxwell' first thermodynamical relation.

## Second Relation :

Put $x = T$ and $y = V$ in equation (6.5),

then

$$\frac{\partial T}{\partial x} = 1 \quad , \quad \frac{\partial V}{\partial y} = 1$$

and

$$\frac{\partial T}{\partial y} = 0 \quad , \quad \frac{\partial V}{\partial x} = 0$$

Substituting in equation (6.5), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots(i$$

This is Maxwell's second thermodynamical relation.

## Third Relation:

Put $x = S$ and $y = P$, in equation (6.5) then

$$\frac{\partial S}{\partial x} = 1, \frac{\partial P}{\partial y} = 1, \frac{\partial S}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$

Substituting these in equation (6.5), we get

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots(i$$

This is Maxwell's third thermodynamical relation

### Fourth Relation:

Put $x = T$ and $y = P$, then equation (6.5) gives

$$\frac{\partial T}{\partial x} = 1, \frac{\partial P}{\partial y} = 1, \frac{\partial T}{\partial y} = 0 \text{ and } \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (6.5), we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(6.9)$$

This is Maxwell's fourth thermodynamical relation. These are the four Maxwell's fundamental thermodynamic relations.

Further there are two more relations within the mechanical variables ($P$, $V$) and thermal variables ($T$, $S$).

### Fifth Relation:

Put $x = P$ and $y = V$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0 \text{ and } \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (6.5), we get

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1 \qquad ...(6.10)$$

### Sixth Relation:

Put $x = T$ and $y = S$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0 \text{ and } \frac{\partial S}{\partial x} = 0$$

Substituting in equation (6.5), we get

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \qquad ...(6.11)$$

Out of these six thermodynamic relations, the one suited for a particular problem is used and the problem is solved. Let us see, some of the important applications of these Maxwell's thermodynamic relations.