Maxwell Thermodynamic relation

Third Thermodynamic relation

$(dP/dT)_V = (dS/dV)_T$

Proof : In terms of Helmholtz free energy (A) , the equation is defined as $A = U - TS$

Differentiating this we get

$dA = dU - TdS - SdT$

$= -PdV - SdT$, (4)

Eq(1) gives

$dU - TdS = -PdV$.

In (4) A is a function of independent variables V and T . Since dA is an exact differential , it follows from (4)

$P = -(dA/dV)_T$

$S = -(dA/dT)_V$

and

$(dP/dT)_V = (dS/dV)_T$

This is called third Maxwell thermodynamic relation .

Fourth thermodynamic relation

$$(dV/\,dT\,)_P \quad = -\,(dS/dP)_T$$

Proof : In terms of Gibb's function G is defined as

$$G = U - TS + PV \;\; = A + PV$$

On differentiating we get

$$dG = dA + PdV + VdP\,,$$

Using (4) it can be written as

$$dG = VdP - SdT\,, \qquad (5)$$

where G is a function of independent variables P and T .In this case dG is an exact differential , so that we find

$$V = (dG/dP)_T$$

$$S = -(dG/dT)_P \qquad (6)$$

and

$$(dV/dT)_P = -(dS/dP)_T$$

This is called Maxwell fourth thermodynamic relation .