For a simple fluid system of fixed size (i.e. fixed N) there are four thermodynamic potentials :-

i) Internal energy U
ii) Enthalpy $H = U + pV$
iii) Helmholtz Free Energy $F = U - TS$
iv) Gibbs Free Energy $G = U - TS + pV$

By analogy with U and H :-

$$\begin{aligned} \mathrm{d}F &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\ &= -p\mathrm{d}V - S\mathrm{d}T \end{aligned}$$

Hence $F = F(T,V)$ i.e. T and V are the natural variables of F.

Also $\left(\frac{\partial F}{\partial V}\right)_T = -p \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$ hence

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

3rd Maxwell Relation

Since $\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$ the change in F represents the work done on/by a system during an isothermal ($\mathrm{d}T = 0$) process.

Also, $\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T$ in general, but $T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V$ only for changes between equilibrium states. For changes between non-equilibrium states $T\mathrm{d}S > \mathrm{d}U + p\mathrm{d}V$ [recall example sharing 14ε between 2 ensembles. $\mathrm{d}U = \mathrm{zero}$ (total energy constant), $\mathrm{d}V = \mathrm{zero}$ (fixed energy levels) but $\mathrm{d}S > 0$ except when equilibrium reached]. Hence $\mathrm{d}F = \mathrm{zero}$ when equilibrium reached, $\mathrm{d}F < \mathrm{zero}$ as equilibrium is approached. Hence

For a system evolving at constant volume and temperature, equilibrium corresponds to a minimum of the system's Helmholtz free energy.

$$\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p$$
$$= -S\mathrm{d}T + V\mathrm{d}p$$

Hence $G = G(T, p)$ i.e. T and p are the natural variables of G.

Also $\left(\frac{\partial G}{\partial p}\right)_T = V \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$ hence

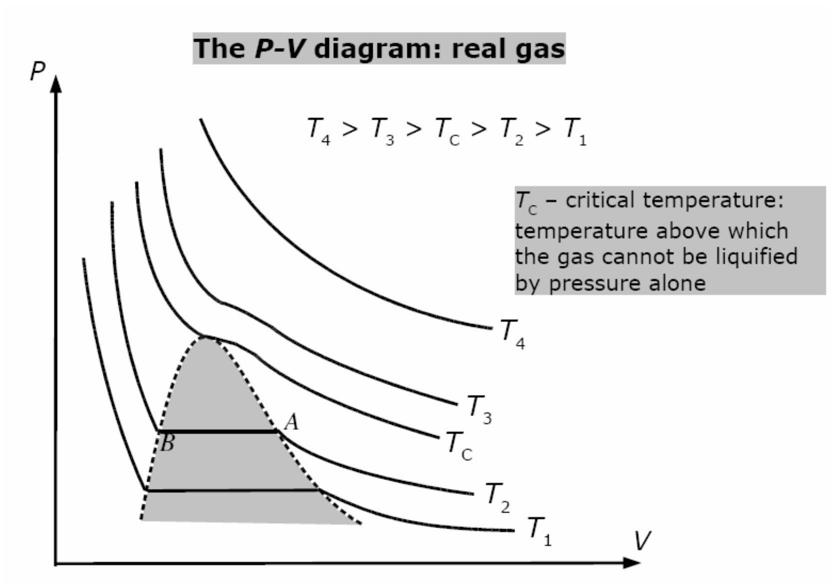
$$\boxed{\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T}$$

4th Maxwell Relation

By analogy with F :-

For a system evolving at constant pressure and temperature, equilibrium corresponds to a minimum of the system's Gibbs free energy.

For a reversible process occurring at constant pressure and temperature (e.g. a phase change between gas and liquid such as from *A* to *B* in the figure below), the Gibbs Free Energy is a conserved quantity.



THERMODYNAMIC POTENTIALS AND MAXWELL RELATIONS SUMMARY TABLE

Potential	Natural variables	Maxwell Relation
U	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H = U + pV$	S, p	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$F = U - TS$	T, V	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
$G = U - TS + pV$	T, p	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$