

Lecture 10
Maxwell's Relations and Their
Applications

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Spontaneity and Equilibrium In Isolated and non-Isolated Systems

	Thermodynamic state of system	Thermodynamic potential	Direction of spontaneous change in state	Condition of equilibrium
Isolated system	S, V, N U, V, N	U S	Decrease in U Increase in S	Minimization of U Maximization of S
System + Thermostat	T, V, N	$F = U - TS$	Decrease of F	Minimization of F
System + Thermostat + Barostat	T, p, N	$G = U - TS + pV$	Decrease of G	Minimization of G

Maximization of Entropy

$$S = S(U, V)$$

At equilibrium

$$\left(\frac{\partial S}{\partial V}\right)_U = 0 \text{ and } \left(\frac{\partial^2 S}{\partial V^2}\right)_U < 0$$

What happens to **internal energy** when entropy is a maximum?

$$U = U(S, V)$$

At equilibrium

$$\left(\frac{\partial U}{\partial V}\right)_S = 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S > 0$$

Combining the 1st and 2nd law of thermodynamics

$$\text{1st law: } dU = \delta q + \delta w$$

$$\text{2nd law: } TdS \geq \delta q$$

$$TdS \geq dU - \delta w$$

$$\text{At Equilibrium} \rightarrow TdS = dU + p dV$$

$$\text{For } \delta w = -pdV$$

$$dU = TdS - p dV$$

Internal Energy Thermodynamic Potential of an Isolated System

Internal Energy,

$$dU = TdS - pdV \quad U = U(S, V, N)$$

Enthalpy, $H = U + pV$

$$dH = TdS + Vdp$$

$$H = H(S, p, N)$$

Helmholtz free energy, $F = U - TS$

$$dF = -SdT - pdV$$

$$F = F(T, V, N)$$

Gibbs free energy, $G = U - TS + pV$

$$dG = -SdT + Vdp$$

$$G = G(T, p, N)$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} \quad -p = \left(\frac{\partial U}{\partial V} \right)_{S, N}$$

We shall fill in the blanks for other energy function just in a bit.

System	Equilibrium state	Thermodynamic potential	Thermodynamic equation of state
Isolated	S, V, N	$U = U(S, V, N)$	$dU = TdS - pdV$

System + Thermostat	T, V, N	$F = U - TS$ $F = F(T, V, N)$	$dF = -SdT - pdV$
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System+ Barostat	S, p, N	$H = U + pV$ $H = H(S, p, N)$	$dH = TdS + Vdp$
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System + Thermostat + Barostat	T, p, N	$G = U - TS + pV$ $G = G(T, p, N)$	$dG = -SdT + Vdp$
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Thermodynamic potentials as exact state functions in closed systems

For a **state function**, $A(x, y)$, dA is an **exact differential**

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

$$dA = M(x, y)dx + N(x, y)dy$$

$dA = \left(\frac{\partial A}{\partial x} \right)_y dx + \left(\frac{\partial A}{\partial y} \right)_x dy$	$M = \left(\frac{\partial A}{\partial x} \right)_y$	$N = \left(\frac{\partial A}{\partial y} \right)_x$
$dU = TdS - pdV$	$T = \left(\frac{\partial U}{\partial S} \right)_V$	$-p = \left(\frac{\partial U}{\partial V} \right)_S$
$dH = TdS + Vdp$	$T = \left(\frac{\partial H}{\partial S} \right)_p$	$V = \left(\frac{\partial H}{\partial p} \right)_S$
$dF = -SdT - pdV$	$-S = \left(\frac{\partial F}{\partial T} \right)_V$	$-p = \left(\frac{\partial F}{\partial V} \right)_T$
$dG = -SdT + Vdp$	$-S = \left(\frac{\partial G}{\partial T} \right)_p$	$V = \left(\frac{\partial G}{\partial p} \right)_T$

Thermodynamic potentials as exact state functions

For a **state function**, $A(x, y)$, dA is an **exact differential** of the form

$$dA = M(x, y) dx + N(x, y) dy \text{ such that}$$

Schwarz's theorem

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$dA = M(x, y) dx + N(x, y) dy$	$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$
$dU = TdS - pdV$	$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$
$dH = TdS + Vdp$	$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}$
$dF = -SdT - pdV$	$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}$
$dG = -SdT + Vdp$	$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}$

Maxwell's relations

Using Thermodynamic Potentials in Real Systems

Give them a **Sp**or**Ti**Ve chance!



1st move

(-)ve

Horizontal

(+)ve

Vertical

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

Maxwell's relations

Applications of Maxwell's Relations

Calculations of Response function:

- From First Law: $dU = -PdV + TdS$ with respect to V at constant T :

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T$$

- Equations should be expressed in terms of P , V , T .

From Maxwell's relation we know $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$

Hence, $\left(\frac{\partial u}{\partial v}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$

Expression of $\bar{c}_p - \bar{c}_v$:

We have by definition, $\bar{c}_p - \bar{c}_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$

$$\text{But, } H = U + PV \text{ or } \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{Hence, } \bar{c}_p - \bar{c}_v = \left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V + P \left(\frac{\partial V}{\partial T}\right)_P$$

But, $U = f(T, V)$ Hence, $du = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

dividing by dT at constant 'P' —

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

$$\text{or, } \left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{Putting the value, } \bar{c}_p - \bar{c}_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{But, thermodynamic equation of state is, } \boxed{P + \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V}$$

$$\text{Hence, } \boxed{\bar{c}_p - \bar{c}_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

This is the general expression of $\bar{c}_p - \bar{c}_v$ for any system, ideal or real and is valid also for condensed system.

Application of maxwell's relation on the van der Waals Equation of State

$$\left(\frac{\partial u}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V$$

For a **Van der Waals gas**, the equation of state is:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Taking the **partial derivative with respect to T at constant V** :

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

Substituting this into the earlier equation:

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T \cdot \frac{nR}{V - nb} - \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) \\ &= \frac{TnR}{V - nb} - \frac{nRT}{V - nb} + \frac{an^2}{V^2} \\ &= \frac{an^2}{V^2}\end{aligned}$$