

## Maxwell Relations

Follow from 2<sup>nd</sup> derivatives of the thermodynamic potentials  
Energy:

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

$$\text{so } \left( \frac{\partial^2 E}{\partial S \partial V} \right)_N = \left( \frac{\partial T}{\partial V} \right)_{S, N}$$

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

$$\text{so } \left( \frac{\partial^2 E}{\partial V \partial S} \right)_N = - \left( \frac{\partial p}{\partial S} \right)_{V, N}$$

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

Can do the same for any thermodynamic potential  
Helmholtz free energy

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

$$\text{so } - \left( \frac{\partial^2 A}{\partial T \partial V} \right)_N = \left( \frac{\partial S}{\partial V} \right)_{T, N}$$

$$\text{but: } - \left( \frac{\partial A}{\partial V} \right)_{T, N} = p(T, V, N)$$

$$\text{so } - \left( \frac{\partial^2 A}{\partial V \partial T} \right)_N = \left( \frac{\partial p}{\partial T} \right)_{V, N}$$

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

Or Gibbs free energy

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

$$\text{so } \left( \frac{\partial^2 G}{\partial p \partial N} \right)_T = \left( \frac{\partial V}{\partial N} \right)_{T, p}$$

$$\text{but } \left( \frac{\partial G}{\partial N} \right)_{T, p} = \mu(T, p, N)$$

$$\text{so } \left( \frac{\partial^2 G}{\partial N \partial p} \right)_T = \left( \frac{\partial \mu}{\partial p} \right)_{T, N}$$

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

These equivalences, which follow from the independence of the order of taking 2nd derivatives, are called the Maxwell Relations

See Callen Chpt 7 for a complete list

## Response functions

specific heat at const volume  $C_V = \left(\frac{dQ}{dT}\right)_{V,N} = T \left(\frac{dS}{dT}\right)_{V,N}$

specific heat at const pressure  $C_P = \left(\frac{dQ}{dT}\right)_{P,N} = T \left(\frac{dS}{dT}\right)_{P,N}$

isothermal compressibility  $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,N}$

adiabatic compressibility  $\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{S,N}$

coefficient of thermal expansion  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N}$

All the above may be viewed as a second derivative of an appropriate thermodynamic potential

$$C_V = T \left(\frac{dS}{dT}\right)_V = -T \left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} \quad \text{since } \left(\frac{\partial A}{\partial T}\right)_{V,N} = -S(T, V, N)$$

$$C_P = T \left(\frac{dS}{dT}\right)_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \quad \text{since } \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S(T, P, N)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \quad \text{since } \left(\frac{\partial G}{\partial P}\right)_{T,N} = V(T, P, N)$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S = -\frac{1}{V} \left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \quad \text{since } \left(\frac{\partial H}{\partial P}\right)_{S,N} = V(S, P, N)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial P}\right)_{N} \quad \text{since } \left(\frac{\partial G}{\partial P}\right)_{T,N} = V(T, P, N)$$

Since all the various thermodynamic potentials can all be derived from one another, the various second derivatives must ~~all~~ be related. If we consider

cases where  $N$  is held constant (as in all the above response functions) then there ~~are only~~ can be only three independent second derivatives, for example

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P, N} = -C_P/T$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T, N} = -V\kappa_T$$

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right)_N = V\alpha$$

All the other second derivatives of the other potentials must be some combination of these three.

Consider  $C_V$  we will show how to write it in terms of the above.

Consider Helmholtz free energy  $A(T, V)$

since  $N$  is kept constant, we will not write it

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

viewing  $S$  as a function of  $T$ , and  $V$  we have

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

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

$$\Rightarrow C_p = C_v + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p$$

$$\text{Now } \left( \frac{\partial S}{\partial V} \right)_T = - \frac{\partial^2 A}{\partial T \partial V} = \left( \frac{\partial p}{\partial T} \right)_V$$

$$\text{and } \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial p} \right)_T = -1 \quad \leftarrow \text{(see general result next page)}$$

$$\text{So } \left( \frac{\partial p}{\partial T} \right)_V = \frac{-1}{\left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial p} \right)_T} = - \frac{\left( \frac{\partial V}{\partial T} \right)_p}{\left( \frac{\partial V}{\partial p} \right)_T}$$

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

$$= C_v - T \frac{(V\alpha)^2}{-V\kappa_T} = C_v + T V \frac{\alpha^2}{\kappa_T}$$

$$\text{So } \boxed{C_v = C_p - \frac{T V \alpha^2}{\kappa_T}}$$

## A general result for partial derivatives

Consider any three variables satisfying a constraint

$$f(x, y, z) = 0 \quad \Rightarrow \quad z \text{ for example, is function of } x \text{ and } y \\ \text{or } y \text{ is function of } x, z \text{ etc.}$$

$\Rightarrow$  exists a relation between partial derivatives of the variables with respect to each other.

$$\text{constraint} \Rightarrow df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = 0$$

if hold  $z$  const, i.e.  $dz = 0$ , then

$$\left(\frac{\partial x}{\partial y}\right)_z = - \frac{(\partial f / \partial y)_{x,z}}{(\partial f / \partial x)_{y,z}}$$

if hold  $y$  const, i.e.  $dy = 0$ , then

$$\left(\frac{\partial z}{\partial x}\right)_y = - \frac{(\partial f / \partial x)_{y,z}}{(\partial f / \partial z)_{x,y}}$$

if hold  $x$  const, i.e.  $dx = 0$ , then

$$\left(\frac{\partial y}{\partial z}\right)_x = - \frac{(\partial f / \partial z)_{x,y}}{(\partial f / \partial y)_{x,z}}$$

Multiplying together we get

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$(x, y, z)$  with constraint among them

Solve for  $x(y, z)$  or for  $y(x, z)$

$$\text{then } dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad (1)$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \quad (2)$$

Suppose vary  $x$  keeping  $dz = 0$

$$(1) \Rightarrow dx = \left(\frac{\partial x}{\partial y}\right)_z dy \Rightarrow \frac{dy}{dx} = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}$$

$$(2) \Rightarrow dy = \left(\frac{\partial y}{\partial x}\right)_z dx \Rightarrow \frac{dy}{dx} = \left(\frac{\partial y}{\partial x}\right)_z$$

$$\Rightarrow \boxed{\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}}$$

Similarly we must be able to write  $\kappa_s$  in terms of  $C_p, \kappa_T, \alpha$

Consider enthalpy  $H(S, P)$

$$\left(\frac{\partial H}{\partial P}\right)_S = V(S, P)$$

regarding  $V$  as a function of  $S$  and  $P$  we have

$$dV = \left(\frac{\partial V}{\partial P}\right)_S dP + \left(\frac{\partial V}{\partial S}\right)_P dS$$

$$-\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S - \frac{1}{V} \left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T$$

$$\kappa_T = \kappa_S - \frac{1}{V} \left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T$$

$$\text{Now } \left(\frac{\partial S}{\partial P}\right)_T = \frac{-\partial^2 G}{\partial T \partial P} = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{and } \left(\frac{\partial V}{\partial S}\right)_P = \frac{(\partial V / \partial T)_P}{(\partial S / \partial T)_P}$$

above follows from:  $\frac{\partial G}{\partial P} = V(T, P) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$$-\frac{\partial G}{\partial T} = S(T, P) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_P}$$

or in general, if  $z$  and  $y$  are functions of  $u$  and  $x$ , i.e.  $z(u, x), y(u, x)$  then  $\left(\frac{\partial z}{\partial y}\right)_x = \frac{(\partial z / \partial u)_x}{(\partial y / \partial u)_x}$



substitute in to get

$$K_T = K_S + \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial S}{\partial T} \right)_P} = K_S + \frac{1}{V} \frac{(V\alpha)^2}{C_P/T}$$

$$K_T = K_S + \frac{TV\alpha^2}{C_P}$$

$$K_S = K_T - \frac{TV\alpha^2}{C_P}$$

See Callen for a systematic way to reduce all such derivatives to combinations of  $C_P$ ,  $K_T$ ,  $\alpha$

The main point is not to remember how to do this, but that it can be done! There are only a finite number of independent 2<sup>nd</sup> derivatives of the thermodynamic potentials! [if consider only mass  $N$  fixed, there are only  $C_P$ ,  $K_T$ ,  $\alpha$ ]

Another useful relation

$$C_V = T \left( \frac{dS}{dT} \right)_V$$

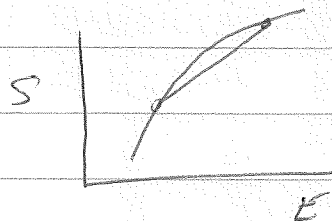
Since  $dE = TdS - PdV$  ( $N$  fixed)  
it follows that

$$C_V = \left( \frac{dE}{dT} \right)_V = T \left( \frac{dS}{dT} \right)_V$$

## Stability

We already saw that the condition of stability required that  $S(E)$  be a concave function

$$\frac{\partial^2 S}{\partial E^2} \leq 0$$



concave  $\equiv$  the cord drawn between any two points on curve lies below the curve

In a similar way, one can show  $\frac{\partial^2 S}{\partial V^2} \leq 0$ ,

or more generally,  $S$  is concave in three dimensional  $S, E, V$  space

$$S(E + \Delta E, V + \Delta V, N) + S(E - \Delta E, V - \Delta V, N) \leq 2S(E, V, N)$$

expanding the ~~right~~<sup>left</sup> hand side in a Taylor series we get

$$\frac{\partial^2 S}{\partial E^2} \Delta E^2 + 2 \frac{\partial^2 S}{\partial E \partial V} \Delta E \Delta V + \frac{\partial^2 S}{\partial V^2} \Delta V^2 \leq 0$$

For  $\Delta V = 0$  this gives  $\frac{\partial^2 S}{\partial E^2} < 0$

For  $\Delta E = 0$  this gives  $\frac{\partial^2 S}{\partial V^2} < 0$

More generally, for  $\Delta E$  and  $\Delta V$  both  $\neq 0$ , we can rewrite as

$$(\Delta E, \Delta V) \begin{pmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E \partial V} \\ \frac{\partial^2 S}{\partial E \partial V} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix} \begin{pmatrix} \Delta E \\ \Delta V \end{pmatrix} \leq 0$$

both eigenvalues of the matrix must be  $\leq 0$

That the quadratic form is always negative implies that  
and so the determinant of the matrix ~~is negative~~ <sup>must be</sup> positive  $\geq 0$

$$\frac{\partial^2 S}{\partial E^2} \frac{\partial^2 S}{\partial V^2} - \left( \frac{\partial^2 S}{\partial E \partial V} \right)^2 \geq 0$$

$$\text{Note: } \left( \frac{\partial^2 S}{\partial E^2} \right)_V = \frac{\partial}{\partial E} \left( \frac{1}{T} \right)_V = -\frac{1}{T^2} \left( \frac{\partial T}{\partial E} \right)_V = \frac{-1}{T^2 C_V}$$

$$\text{So } \left( \frac{\partial^2 S}{\partial E^2} \right)_V \leq 0 \Rightarrow C_V \geq 0 \quad \text{specific heat is positive}$$

### Other Potentials

One can use the minimization principles of the other thermodynamic potentials,  $E, A, G$ , etc to derive other stability criteria.

### Energy

$S$  is maximum  $\Rightarrow E$  is minimum

$S$  concave  $\Rightarrow E$  is convex

$$\Rightarrow E(S + \Delta S, V + \Delta V, N) + E(S - \Delta S, V - \Delta V, N) \geq 2E(S, V, N)$$

$$\Rightarrow \left( \frac{\partial^2 E}{\partial S^2} \right)_V = \left( \frac{\partial T}{\partial S} \right)_V \geq 0 \quad \text{and} \quad \left( \frac{\partial^2 E}{\partial V^2} \right)_S = - \left( \frac{\partial P}{\partial V} \right)_S \geq 0$$

$$\text{and} \quad \left( \frac{\partial^2 E}{\partial S^2} \right)_V \left( \frac{\partial^2 E}{\partial V^2} \right)_S - \left( \frac{\partial^2 E}{\partial S \partial V} \right)^2 \geq 0$$

$$\text{or} \quad - \left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial P}{\partial V} \right)_S - \left( \frac{\partial T}{\partial V} \right)_S^2 \geq 0$$

$$\text{using } \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}, \quad \left(\frac{\partial P}{\partial V}\right)_S = -\frac{1}{V\kappa_S}, \quad \left(\frac{\partial T}{\partial V}\right)_S$$

we get

$$\frac{T}{V C_V \kappa_S} \approx \left(\frac{\partial T}{\partial V}\right)_S^2$$