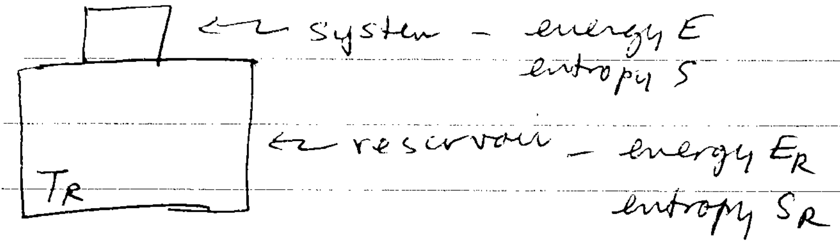
Consider a system in contact with a thermal reservoir

Only energy can be exchanged between system + reservoir

Temperature T_R of reservoir is const by definition



Since system is in equilib with reservoir, the system temp $T = T_R$

If an internal constraint in the system is relaxed, what determines ~~the~~ new equilib state?

Use entropy formulation - total energy is conserved $E^{tot} = E_R + E$

total entropy is maximized

$$S^{tot} = S_R(E_R) + S(E)$$
$$= S_R(E^{tot} - E) + S(E)$$

Since $E \ll E^{tot}$ (as $E_R \gg E$ by def of reservoir)

we can expand

$$S^{tot} \simeq S_R(E^{tot}) - \left(\frac{\partial S_R}{\partial E_R}\right) E + S(E)$$

$$= S_R(E^{tot}) - \frac{E}{T_R} + S(E)$$

$$= S_R(E^{tot}) - (E - T_R S)/T_R \qquad T_R = \underset{\substack{\uparrow \\ \text{system} \\ \text{temp}}}{T}$$

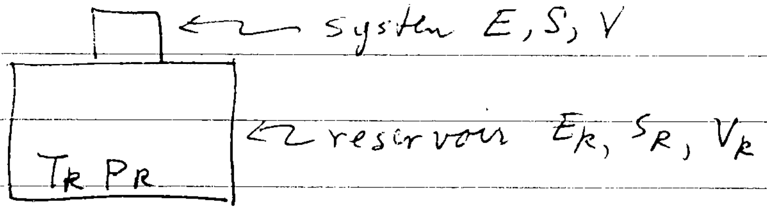
$$= \underset{\substack{\uparrow \\ \text{constant}}}{S_R(E^{tot})} - \underset{\substack{\nearrow \\ \text{Helmholtz free energy}}}{A}/T_R$$

S^{tot} maximized $\Rightarrow$ A minimized

$\Rightarrow$ the equilib. state of a system in contact with a thermal reservoir will be the one the minimizes the Helmholtz free energy $A(T, V, N)$

Now consider a system in contact with a thermal + pressure reservoir

pressure reservoir always has fixed pressure p_R



total energy conserved $E^{tot} = E_R + E$ = constant
total volume conserved $V^{tot} = V_R + V$ = const

system in equilib with reservoir $\Rightarrow$ $T = T_R$, $p = p_R$

$$S^{tot} = S_R(E_R, V_R) + S(E, V)$$

$$= S_R(E^{tot} - E, V^{tot} - V) + S(E, V)$$

$$\simeq S_R(E^{tot}, V^{tot}) - \left(\frac{\partial S_R}{\partial E_R}\right) E - \left(\frac{\partial\ _R}{\partial V_R}\right) V + S(E, V)$$

$$= \text{constant} - \frac{E}{T_R} - \frac{P_R}{T_R} V + S$$

$$= \text{const} - (E + pV - ST)/T = \text{const} - G/T$$

S^{tot} maximized $\Rightarrow$ G, Gibbs Free energy is minimized

⇒ the equilb state of a system in contact with a thermal + pressure reservoir will be the one that minimizes the Gibbs free energy $G(T, p, N)$

Similarly - the equilb state of a system in contact with a pressure reservoir will be the one that minimizes the enthalpy $H(S, p, N)$

and - the equilb state of a system in contact with a thermal and a particle reservoir (a particle reservoir can exchange particles with the system, but is so large that its chemical potential μ_R stays constant) will be the one that minimizes the grand potential $\Sigma(T, V, \mu)$

Maxwell Relations

Follow from 2nd 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 <u>Gibbs free energy</u>

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

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

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

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

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

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

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

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

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

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

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

$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial p}\right)_N$ 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 derivates must ~~[illegible]~~ 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 derivates, 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

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

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

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

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

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

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

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

$$= C_V - T\frac{(V\alpha)^2}{-V K_T} = C_V + \frac{TV\alpha^2}{K_T}$$

So $$\boxed{C_V = C_p - \frac{TV\alpha^2}{K_T}}$$

A general result for partial derivatives

Consider any three variables satisfying a constraint

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

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

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, ie $dz = 0$, 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, ie $dy = 0$, then

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

if hold x const, ie $dx = 0$, 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

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

Similarly we must be able to write κ_S in terms of c_p, κ_T, α

Consider enthalpy $H(S, p)$

$$\frac{\partial H}{\partial p} = V(S, p)$$

regarding V as a function of S and p we have

$$dV = \left(\frac{\partial V}{\partial p}\right)_S dp + \left(\frac{\partial V}{\partial S}\right)_p dS$$

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

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

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

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 $\left(\frac{\partial z}{\partial y}\right)_x = \frac{(\partial z/\partial u)_x}{(\partial y/\partial u)_x}$

substitute in to get

$$\kappa_T = \kappa_S + \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_p} = \kappa_S + \frac{1}{V}\frac{(V\alpha)^2}{C_p/T}$$

$$\kappa_T = \kappa_S + \frac{TV\alpha^2}{C_p}$$

$$\boxed{\kappa_S = \kappa_T - \frac{TV\alpha^2}{C_p}}$$

See Callen for a systematic way to reduce all such derivatives to combinations of C_p, κ_T, α

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 2nd derivatives of the thermodynamic potentials! [if consider only ~~mass~~ N fixed, there are only C_p, κ_T, α]

Another useful relation

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

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

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